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Selective oxidation of C₄ hydrocarbons over (VO)₂P₂O₇ catalyst: Nature of the redox mechanism

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Nature of the redox mechanism**

Kamat, Satish Naravan, Ph.D.

Iowa State University, 1992

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Selective oxidation of C₄ hydrocarbons over (VO)₂P₂O₇ catalyst:

Nature of the redox mechanism

by

Satish Narayan Kamat

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

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**Iowa State University
Ames, Iowa**

1992

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GENERAL INTRODUCTION

The chemical utilization of alkanes is a relatively new and exciting area of the selective oxidation catalysis. Light alkanes such as n-butane are available abundantly, and transformation of these cheap, but rather inert, alkanes into either gasoline range hydrocarbons or petrochemical intermediates is highly desirable. One of the few industrial processes using this type of chemistry is the conversion of n-butane to maleic anhydride. Maleic anhydride has found a variety of uses, including food additives, plasticizers and agricultural chemicals [1].

The industrial catalyst for this process is a vanadium phosphorus oxide (V-P-O) catalyst [2]. A wide variety of V-P-O phases have been investigated, but it is generally accepted that vanadyl pyrophosphate, $(VO)_2P_2O_7$ (V^{4+}) is present in the industrial catalysts as the most active and selective phase [3-11]. Many studies have correlated the catalytic performance of these catalysts with the preparation and activation techniques. These studies demonstrated the importance of P-to-V ratio [4-7, 12-20], oxidation state [21-27], and structural characteristics [28-34]. More recently, investigations have focused on the detection of the possible intermediates in the reaction pathways, the role of different oxygen species, and the nature of the active sites involved in the redox mechanism. In general, these studies have made significant contributions to the understanding of V-P-O catalysts. However, as discussed latter in following sections, there are a number of discordances in this literature.

Particularly, the polyfunctional nature of these catalysts, along with the presence of various types of oxygen species in this catalytic system has made it very difficult to investigate the nature of the active oxygen species as well as its availability for selective and nonselective oxidation pathways. Thus, in general, the redox mechanism is not well understood in terms of the oxygen species.

This dissertation is a report of research completed with the prime objective of investigating the redox mechanism operating in the vanadyl pyrophosphate catalyst for the selective oxidation of C_4 hydrocarbons. Previous research has established the general redox behavior of V-P-O catalysts; a Mars-van Krevelan type mechanism has been proposed involving V^{4+} and V^{5+} oxidation states [11]. A two-part approach was employed in this investigation. First the role of various surface layer oxygen, and the participation of bulk oxygen in the redox behavior of $(VO)_2P_2O_7$ was studied. This was achieved by determining the reactivities of these oxygen species and their replenishment from the bulk lattice. In the second part, the interaction of the gas-phase oxygen with the catalyst surface was studied to understand the nonselective pathways, nature of oxygen species involved, and the catalyst reoxidation mechanism.

In the following sections of this introduction, a detailed review of the past research work concerning this work, the objectives of the research, and the explanation of the dissertation format are presented.

Literature Review

In this section, an outline of the literature concerning the mechanism of n-butane conversion to maleic anhydride over V-P-O catalysts is presented. Because of the industrial importance of this processing route, V-P-O catalysts have been investigated extensively in the last few years. A number of general review articles have appeared on this topic, covering the areas of n-butane activation, intermediates involved, influence of the P-to-V ratio, oxidation state, etc. [2, 35, 36]. These topics will not be discussed here at length. However, work concerning the active and selective oxygen in this catalyst is particularly important for a detailed understanding of the redox mechanism, and forms the basis of any further work in this area. Hence, it is reviewed in detail.

n-Butane Conversion to Maleic Anhydride over V-P-O Catalyst

Saturated paraffins, such as n-butane are relatively stable hydrocarbons. As a result, their direct chemical utilization has been very limited. Due to their large abundance and cheap cost, they are an attractive source as primary feedstock for petrochemical industry. The challenge here lies in activating n-butane in such a manner as to insert oxygen to produce valuable oxygenates, yet to minimize its complete combustion to carbon oxides. V-P-O catalysts have accomplished this with high yields in industrial reactors. The most important phase for studies of this reaction has been $(VO)_2P_2O_7$, though other phases have also been

investigated, viz. β -VOPO₄. The work reviewed here deals mostly with the n-butane oxidation over these phases.

Reaction Pathways

The first step in n-butane conversion to maleic anhydride is obviously the activation of n-butane on the catalyst surface. Activation of n-butane can be broken down into two types: C-H bond activation and C-C bond activation. Since the C-C bond activation would lead to cracking and nonselective products, most work to date deals with the activation of C-H bond.

Experiments by Pepera et al. [11] with deuterated n-butane over (VO)₂P₂O₇ catalyst suggested that the rate determining step is the activation of n-butane through abstraction of one of the methylene hydrogen. They further postulated that the n-butane is chemisorbed and activated in an irreversible and a very specific manner. It was also suggested that both the selective and nonselective routes are initiated through this mode of activation. The irreversibly chemisorbed species was believed to be stabilized at the site of chemisorption, and it was believed that no species are desorbed until the final products (maleic anhydride or carbon oxides) are formed.

The catalyst used in these studies was prepared by calcining the vanadyl hydrogen phosphate hemihydrate phase (obtained through an organic synthesis) in air at 400 C. It was then activated by reaction of n-butane/air mixture at 400 C for 24 h. This catalyst is known as equilibrated catalyst.

These results are in good agreement with the conclusions of the kinetic studies of the oxidation of various C_1 - C_7 hydrocarbons over a $(VO)_2P_2O_7$ catalyst synthesized in a similar fashion. Based on these studies, Centi and Trifiro [37] proposed that the activation of n-butane on the V-P-O catalysts involves the contemporaneous removal of two of the four methylene hydrogens to form a 2-butene-like surface species.

While the initial activation of the paraffin is a crucial function of these catalysts, it is only the first step of a complicated reaction network. Additionally eight hydrogen atoms must be abstracted, while three oxygen atoms must be inserted before producing maleic anhydride. Several reaction pathways have been proposed for the selective oxidation route, ranging from a simple one (Figure 1) [38-43] to a fairly complicated one (Figure 2). A generally accepted conversion pathway is: n-butane \rightarrow 1-butene \rightarrow 1,3-butadiene \rightarrow furan \rightarrow maleic anhydride [9, 16, 26, 37, 44-46]. Much of the previous work in this area has attempted either to confirm or to deny the presence of these intermediates. However, the specific catalytic sites involved in these primary reaction steps have yet to be identified. Carbon oxides can form through two different routes: either by the direct combustion of the n-butane or by the consecutive combustion of surface intermediates and/or maleic anhydride. Recent work by Ebner and Gleaves [49] using time resolved pulse technique provided the evidence for these two routes to combustion. It was proposed that these two routes represent two modes of n-butane activation. However, the active sites or the adsorbed species (intermediates) involved in these nonselective pathways have not been conclusively determined.

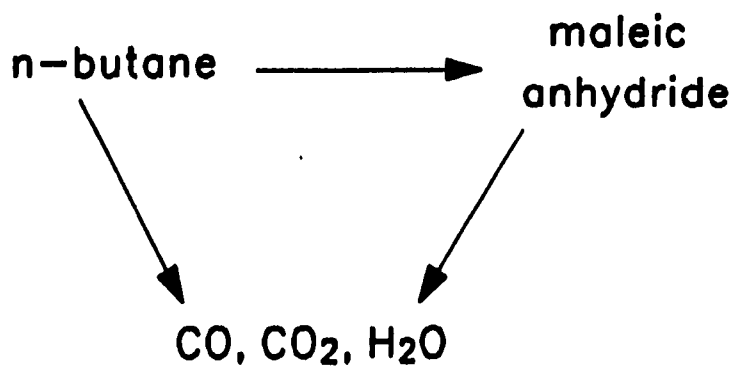


Figure 1: A simple reaction pathway for n-butane oxidation to maleic anhydride [40]

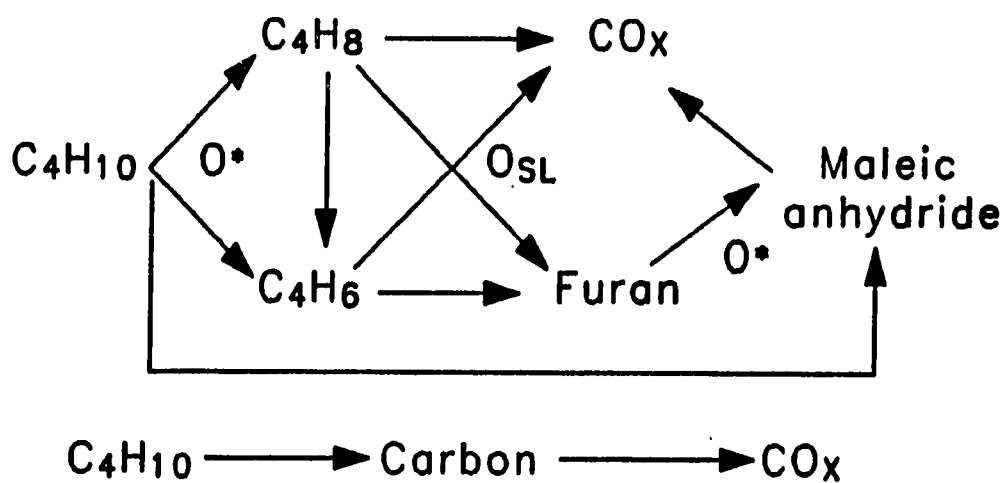


Figure 2: A detailed reaction network for n-butane oxidation to maleic anhydride [49]

To investigate the nature of the active oxygen sites one must first know the various types of oxygen species present in the catalyst. This requires an understanding of the catalyst structure, which is discussed in the following section. The work concerning the role of active and selective oxygen sites for n-butane conversion to maleic anhydride is reviewed in detail in one of the latter sections.

The Structure of $(VO)_2P_2O_7$

The catalytic performance of $(VO)_2P_2O_7$ catalyst has been shown to be a function of the synthesis techniques used. The different synthesis routes lead to different catalyst microstructures. This not only explains the differences in the activities and selectivities of these catalyst, but also indicates the structural sensitivity of this oxidation reaction [31]. Bordes and Courtine have attempted to explain these effects in terms of the two different crystalline phases [22]. β - $(VO)_2P_2O_7$ was proposed to have a network structure, and can be formed either by the reduction of β - $VOPO_4$ through a crystallographic shear mechanism or by the decomposition of vanadyl hydrogen phosphate under n-butane/air reaction mixture at 400 C. γ - $(VO)_2P_2O_7$ forms by the dehydration of vanadyl hydrogen phosphate in air or reduction of γ - $VOPO_4$, and has a layered structure. The x-ray diffraction patterns for these two phases are however, very similar. Recent work by Thompson and Ebner [30] demonstrated that $(VO)_2P_2O_7$ exists in at least two different crystal structures. Using the microcrystalline powder sample of $(VO)_2P_2O_7$ obtained from a fixed-bed reactor after more than 5000 hours of the butane oxidation, these investigators were successful in synthesizing

two types of single crystals of $(VO)_2P_2O_7$. The original microcrystalline powder catalyst was obtained through an aqueous route [31]. These investigators, therefore, suggested that $(VO)_2P_2O_7$ is polymorphic. The two crystal structures were suggested to be related via differing orientation of the vanadyl group in adjacent chains within the structure. Of the two phases obtained, one is the known β -phase, while other phase exhibits lattice parameters which are slightly dilated relative to β - $(VO)_2P_2O_7$. At this time, it is not clear whether the second crystalline phase observed in this study is same as the γ -phase proposed by Border and Courtine [22]. Since the solid state synthesis route to be used for preparing ^{18}O -labeled $(VO)_2P_2O_7$ catalyst leads to a predominantly β - $(VO)_2P_2O_7$ phase, its structure is used as a basis for all discussions in this study.

The crystal structure of the β - $(VO)_2P_2O_7$ phase consists of irregular VO_6 octahedral pairs linked by corner-sharing pyrophosphate ($P_2O_7^{4-}$) tetrahedra. An infinite chain structure is formed through the $V=O \cdots V$ bonding, in which the VO_6 octahedra are linked in pairs through a common edge, forming double chains in this direction [35]. The pyrophosphate ($P_2O_7^{4-}$) groups form two tridentate oxygen bridges with three separate chains, which gives rise to four P-O-V bonds, two $P-O^V-V$ bonds and a P-O-P bond. Only equatorial oxygens in the VO_6 octahedra are shared with the pyrophosphate groups. Figure 3(a) shows the projection of $(VO)_2P_2O_7$ along the [020] plane [35]. The networking between the V octahedra and P tetrahedra within a layer of $(VO)_2P_2O_7$, containing the vanadyl dimer groups is shown in Figure 3(b).

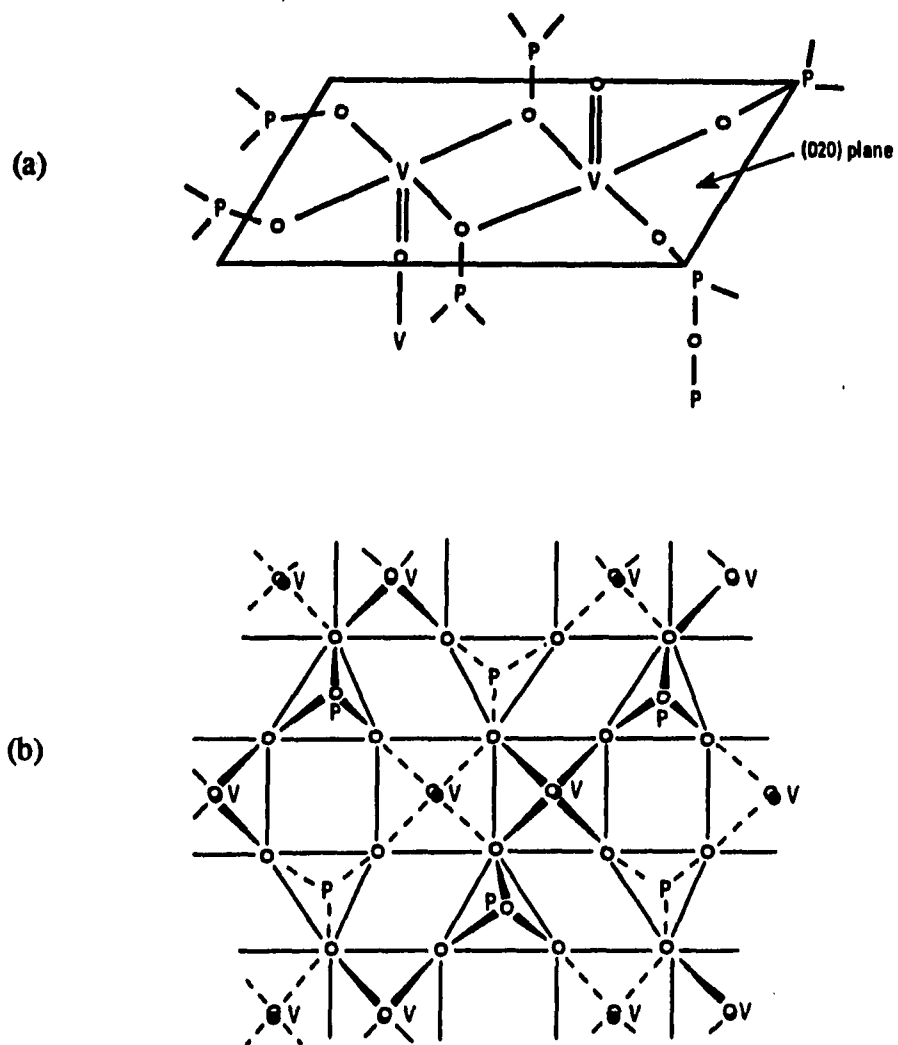
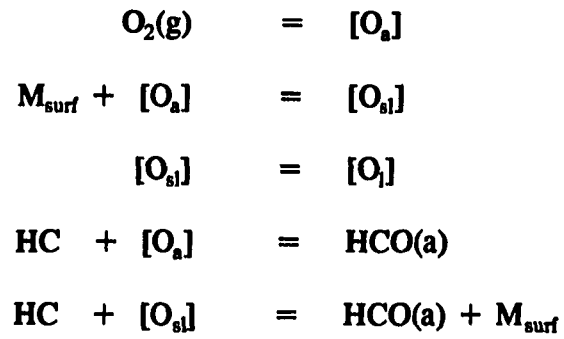


Figure 3: Crystal structure of $(VO)_2P_2O_7$: (a) projection along the $[020]$ plane, and (b) connectivity-V octahedra and P tetrahedra within a layer containing the vanadyl dimer groups [35]

Role of Oxygen

In the catalytic oxidation of hydrocarbons, the presence of oxygen is required for oxygen insertion in the molecule; however, highly reactive oxygen can produce carbon oxides. Thus, it is very important to study the role of various oxygen present in the system. Because of the complex nature of the redox mechanism, it is important first to consider the various possible forms of active oxygen present and the processes involving appearance and disappearance of one or another of these forms. This is generally referred to as the activation of dioxygen, and has been extensively reviewed [47-48]. The generally accepted mechanism for the activation of oxygen on metal oxides is shown in Figure 4. It involves a stepwise process in which the gas-phase molecular oxygen first chemisorbs to form an activated species, $[O_a]$. The irreversibly chemisorbed species can be molecular surface species such as O_2^{2-} or O_2^- , or dissociatively adsorbed monoatomic anions such as O^{2-} or O^- . For $(VO)_2P_2O_7$, it can also be a $V^{5+}-O$ type species as proposed by Ebner and Gleaves [49]. O^- and O_2^- species are known to be very reactive in the oxidative dehydrogenation and activation of lower alkanes [50]. O^{2-} generally shows the least reactivity in alkane activation and is considered as a lattice species. Since all of these species (except O^{2-}) are formed only at the surface defects, their population tends to be very low (1-3 % of surface sites) under reaction conditions. Chemisorbed oxygen may then either react with the hydrocarbon or it may replenish the surface layer oxygen, many times referred as surface lattice oxygen $[O_{sl}]$. The latter one can in turn replenish the bulk oxygen, $[O_b]$, or reacts with the hydrocarbon. It should be noted that surface layer and bulk oxygen, together form the lattice oxygen of



where

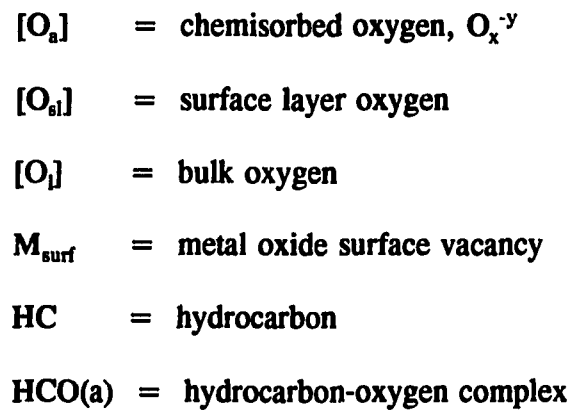


Figure 4: Activation of oxygen over metal oxides [48]

catalyst. This terminology for oxygen species will be used throughout this dissertation. Table 1 lists the various possible oxygen species that can be present in this system. As can be seen from this table, several types of oxygen species can exist at the surface of $(VO)_2P_2O_7$ catalyst. These are: $V=O$, $V-O-P$, $V--O=V$, $V-O^P-V$, $P-O$ and $P-O-P$. Of these oxygen species, the $V-O-P$ is most abundant [35]. All the three major forms of oxygen mentioned above have been the subject of many investigations in this area.

Kruchinin et al. [51] studied the incorporation of the ^{18}O from the gas phase into the oxygenated products over a V-P-O catalyst containing additions of cobalt oxide. The reaction was carried out using a n-butane-to-oxygen molar ratio of 5 at 350 C. Using a closed recirculating system, they demonstrated the involvement of bulk oxygen in the production of maleic anhydride, and carbon dioxide from n-butane. The ^{18}O incorporation was gradual, indicating bulk oxygen was being directly used to produce these products; oxygen uptake from the gas phase into the bulk was also shown to occur. However, no exchange was observed between the gas phase oxygen and the catalyst surface layer oxygen under these conditions.

Similar observations led Pepera and coworkers [11] to postulate that the reaction of n-butane over $(VO)_2P_2O_7$ is a special case of the Mars-van Krevelan type redox mechanism. The classical redox mechanism postulated by Mars and van-Krevelan [52] for naphthalene oxidation over V_2O_5 catalyst, involved the bulk oxidation and reduction of the catalyst. For $(VO)_2P_2O_7$ catalyst, it was postulated that the oxidation and reduction is limited to the near surface layers of the catalyst. The experiments of Pepera et al. [11] involved equilibrating

Table 1: Various possible forms of oxygen species present in $(VO)_2P_2O_7$ system

symbol	oxygen locale	types in which these oxygen exists
$[O_s]$	adsorbed	reversibly :- $O(a)$, $O_2(a)$ irreversibly :- O_x^y
$[O_{sl}]$	surface layer	only surface layer: $V=O$ $V-O$ $P-O$ both surface layer and bulk:
$[O_b]$	bulk	$V=O--V$ $V-O/P-V$ $V-O-P$ $P-O-P$

the surface of $(VO)_2P_2O_7$ with ^{18}O , and then reacting n-butane over the catalyst while the incorporation of ^{18}O into CO_2 was monitored. Based on these observations and the considerations of the several reaction models, they concluded that the redox is limited to near surface layers. Surface oxygen was found to be in rapid exchange. It should be noted, however, that CO_2 can be formed through a number of different routes; thus, general conclusions about the complete redox mechanism cannot be solely based on the results obtained for CO_2 . They also presented evidence for a strongly adsorbed hydrocarbon species that leads to the formation of carbon oxides.

The roles of various oxygen species were also investigated by Ebner and Gleaves [49] for equilibrated $(VO)_2P_2O_7$ catalyst, activated by n-butane/air reaction. Their

thermogravimetric study of oxygen-equilibrated catalyst involved increasing the temperature of the catalyst from room temperature to 500 C at a rate of 15 C/min, in flowing O₂ (20% in He). In these experiments, O₂ chemisorption did not become significant until temperatures near n-butane reaction temperature (400 C) were reached. At about 500 C, the reversible adsorption was limited to about 5 % of monolayer coverage (based on the surface density of V atoms in [020] plane). Irreversible chemisorption of O₂ corresponding to one oxygen molecule per three surface vanadium atoms was observed. The activated chemisorption of an electrophilic dioxygen molecule was suggested to result in the oxidation of the surface V⁴⁺ to V⁵⁺. The chemisorption was suggested to occur via a dissociative pathway on vanadium dimers (V-V). The exact chemical form of this adsorbed oxygen was undetermined; however, it was believed to be a V⁵⁺ surface oxo species (V⁵⁺-O).

The reactivity of irreversibly chemisorbed oxygen species (referred as O* hereafter) was studied by TAP (temporal analysis of products) experiments. TAP reactor system allowed these investigator to study a very small portion of the catalyst surface (1/10000) during a very short pulse, typically with a pulse width of 100 millisecond. These experiments involved pulsing very small amounts of intermediates such as butenes and furan over the catalyst. The catalyst was initially pulsed extensively with oxygen at 450 C to form the O* species. When furan was pulsed over the catalyst, the maleic anhydride yield started at a maximum and decreased to zero within about 80 pulses. When n-butane was pulsed over this catalyst afterwards, no maleic anhydride was observed. For cis-2-butene feed, furan yield started at zero and rose to a maximum and remained there for more than 10,000 pulses.

These observations led authors to suggest that two types of selective oxygen are present at the catalyst surface. The irreversibly adsorbed oxygen species (O^*) was postulated to be responsible for n-butane activation and the oxidation of furan to maleic anhydride. It was believed to be present in relatively low concentrations. The second type of oxygen species was believed to be a surface layer species. This type of oxygen was used for allylic oxydehydrogenation of butenes and for oxygen insertion with ring closure to form furan.

They also demonstrated that if insufficient oxygen of the proper type is available at the surface, intermediates may desorb. It is also worth noting that γ -butyrolactone formation was never detected during C_4 olefin and furan oxidation in TAP transient experiments.

The nature of the non-selective oxygen was investigated using time-resolved pulse studies. These studies involve pulsing ^{18}O /cis-2-butene mixture over the catalyst while monitoring the temporal curves for various isotopes of CO_2 . Two sources of oxygen were believed to exist for the formation of CO_2 : a "fast" source identified as a highly reactive chemisorbed oxygen which reacts with hydrocarbon directly to form CO_2 , and a "slow" source attributed to surface layer oxygen. It was not clear from the study whether the reactive chemisorbed oxygen involved in first route is same as the O^* or some short-lived species. Furthermore, the particular type of surface layer oxygen involved in second route is also not known.

It should be noted that Centi et al. [53] also had suggested that CO_2 can be formed from an adsorbed dioxygen species, based on the blocking of oxygen adsorption sites by

NH_3 . These workers observed that, in this system, CO_2 formation was not inhibited by the site blocking effects of ammonia present in the system. Several authors claim that weakly adsorbed oxygens or those formed at surface defect sites are responsible for carbon oxide production [50].

It was also suggested from the TAP experiments that oxygen surface mobility is very high, although it seems likely that movement of oxygen is primarily through the surface layer. The TAP results are summarized in Figure 2.

Haber and Serwicka [54] have discussed the nature of surface layer oxygen species and the propensity of these species towards specific reactions. In general, they conclude that the reactivities of different surface layer oxygen sites depend upon the atoms bound to the oxygen. Several types of oxygen species exist at the surface of vanadyl pyrophosphate as shown in Table 1. It seems probable to Centi and coworkers [35] that these different types of oxygen species are implicated in the polyfunctional behavior of these catalysts. Thus, without the knowledge of the reactivities of these oxygen species, a complete understanding of this catalytic reaction can not be achieved.

An investigation to determine the reactivity of each type of lattice oxygen will require some method of labeling them in the catalyst and later monitoring their incorporation in the products using this label. Lashier and Schrader [55] employed this basic idea to develop a new method to study the reactivity of the individual lattice oxygen species in the n-butane oxidation with V-P-O catalysts. Using a $\beta\text{-VOPO}_4$ catalyst with ^{18}O incorporated in specific lattice oxygen sites, they examined the reactivities of the different lattice oxygen sites under

anaerobic conditions. The location of the ^{18}O was then determined using laser Raman and infrared spectroscopy. The labeled catalyst was pulsed with hydrocarbons and the products were monitored by mass spectrometry to determine the uptake of ^{18}O . This technique was referred to as isotopic reactive-site mapping (IR-SM).

Their work suggested that irreversibly chemisorbed n-butane is activated on $\beta\text{-VOPO}_4$ to form a partially dehydrogenated species; the reaction of this species with P-O-V sites was postulated to produce a furan-like species. Further oxygen insertion at other P-O-V sites was suggested to produce maleic anhydride, most of which desorbed as a final product. Olefins and furan, in the form of gas-phase species, do not play a major role in this mechanism. Furthermore, this work presented clear evidence for the additional routes to CO_2 other than only the consecutive combustion of maleic anhydride. γ -Butyrolactone was also shown not to be an intermediate. An overview of the reaction mechanism for n-butane conversion to maleic anhydride put forward by these investigators is shown in Figure 5.

This work also showed that initial interaction of n-butane is fundamentally different than that for the 1-butene.

Apart from the experimental studies described above, a few theoretical studies testing the kinetic models for these reactions have also been reported [18, 40, 42, 56]. Ziolkowski et al. [57] have analyzed the oxidation of n-butane and 1-butene on the [100] plane of $(\text{VO})_2\text{P}_2\text{O}_7$, in terms of the crystallochemical model of active sites (CMAS). Analysis involved the heats of adsorption of oxygen, hydrogen and water as well as the heats of their movement along the surface, which allowed them to determine the energetically easiest

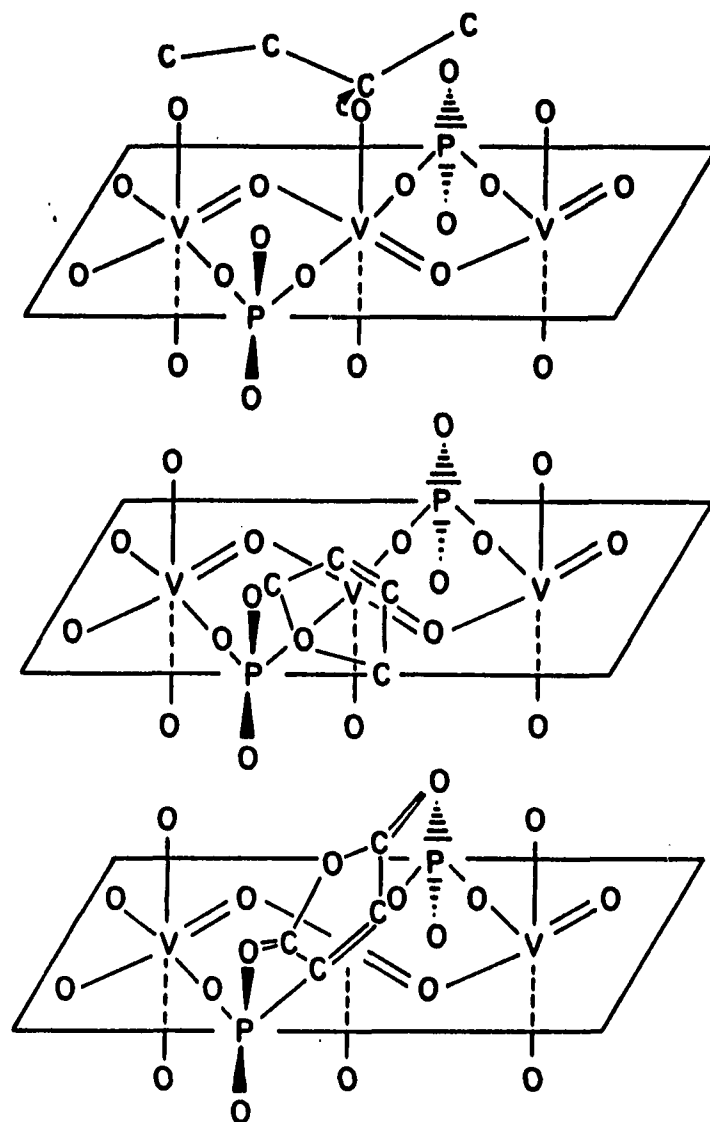


Figure 5: Reaction mechanism for n-butane conversion to maleic anhydride over B-VOPO₄ [55]

pathways of elementary steps and gave insight into the reaction dynamics. The catalyst was found to work only in a surface-oxidized state, all cations being covered with oxygen. Reaction was believed to be initiated by C-H bonding at the methyl groups rather than methylene groups as demonstrated by isotopic studies of Pepera et al. [11]. The active site was postulated to be situated between four protruding, unsaturated oxygens ($2xV-O$, $2xP-O$). The assemblage of unsaturated oxygens around the indicated site was found to be geometrically as well as energetically convenient for both for the abstraction and removal of eight hydrogens and for insertion of three oxygen necessary for the maleic anhydride formation. No mechanism for CO_2 formation was proposed. Although, in general their mechanism is in good agreement with the experimental results, there are some notable disagreements. CMAS model predicted that catalyst works only in surface oxidized state, however, for fresh catalyst, Lashier [58] has reported formation of maleic anhydride under anaerobic conditions. Whereas the model requires monolayer oxygen coverage, O_2 chemisorption studies by Ebner and Gleaves demonstrated less than 16% of monolayer coverage of oxygen at 500 C.

A great deal of information has been amassed on the mechanistic details of this 14-electron oxidation of n-butane to maleic anhydride. However, as summarized in Table 2, there are a number of discordances present in the literature about the nature of the oxygen species involved in the individual steps. Centi et al. [35] have attempted to explain this on the basis of the differences in the catalyst pretreatments. They pointed out that in the fresh catalyst the lattice oxygen is very easily lost due to the presence of defects in the structure.

Table 2: Discordances about the nature of the active oxygen in the conversion of n-butane to maleic anhydride

Proposed Active Oxygen	Catalyst/C ₄ -feed	Reference
1: C-H Activation (n-butane dehydrogenation)		
- V ⁵⁺ ionFs	-VPO ¹ /n-butane	-Hodnett et al. [15]
- V ⁴⁺ -O-P reactive couple	-(VO) ₂ P ₂ O ₇ /n-butane	-Busca et al. [36]
- V ⁵⁺ acid centers	-(VO) ₂ P ₂ O ₇ /n-butane	-Bergeret et al. [24]
- O* irreversibly chemisorbed V ⁵⁺ -O	-(VO) ₂ P ₂ O ₇ /n-butane	-Gleaves et al. [45]
2: Oxydehydrogenation (1-butene -> 1,3-butadiene)		
- V=O	-VPO ¹ /1-butene	-Weiss et al. [59]
- V ⁴⁺ -O-P or V ⁴⁺ =O	-(VO) ₂ P ₂ O ₇ /1-butene	-Centi et al. [60]
3: Oxygen Insertion		
- V ⁵⁺ =O	-(VO) ₂ P ₂ O ₇ /1,3-butadiene	-Centi et al. [60]
- O* irreversibly chemisorbed V ⁵⁺ -O	-(VO) ₂ P ₂ O ₇ /furan	-Gleaves et al. [45]
- P-O-V	-β-VOPO ₄ /n-butane	-Lashier et al. [55]
4: Combustion (C₄ -> CO_x)		
- adsorbed dioxygen	-(VO) ₂ P ₂ O ₇ /NH ₃ /n-butane	-Centi et al. [53]
- O* short-lived adspecies	-(VO) ₂ P ₂ O ₇ /cis-2-butene	-Gleaves et al. [45]
- V=O	-β-VOPO ₄ /n-butane	-Lashier et al. [55]

1: P/V ratios used in these studies were 0.9-1.1.

Thus, the direct oxidation of the hydrocarbon to maleic anhydride can occur in the absence of gas-phase oxygen on a fresh catalyst. With a catalyst activated by n-butane/air reaction, lattice oxygen is not easily labile and can perform only reactions of allylic oxydehydrogenations and oxygen insertion.

In general, the forementioned studies have not only led to better understanding of a very complex polyfunctional catalytic system, but also to possible improvements of the industrial process for this reaction [61]. The latter remark refers to the work of Contractor and coworkers [7] who demonstrated that in the absence of the gas-phase oxygen it is possible to eliminate a highly nonselective oxygen species. Thus by separating the oxidation and reduction functions of the catalyst, they achieved high selectivities for maleic anhydride. The new transport bed technology developed by Du Pont for industrial production of maleic anhydride has made use of this fact. This is an excellent example of how the knowledge of the nature of oxygen species can lead to an improved process technology.

Research Objectives

The prime objective of this research is to investigate the redox mechanism for C_4 hydrocarbon oxidation over $(VO)_2P_2O_7$ catalyst. The redox mechanism will be studied in terms of the role of various oxygen species involved. A two-part approach will be employed to achieve this objective. Initially, the reactivities of individual surface layer oxygen and the participation of the bulk oxygen in the mechanism will be

determined under anaerobic conditions. In the next part, interaction of the gas-phase oxygen with the catalyst surface after reducing it with C₄ hydrocarbons feed will be investigated to study the reoxidation of the reduced catalyst, nonselective pathways and the oxygen species involved. These studies will be carried out with n-butane and 1-butene. The interest in the latter stems from the fact that it is a known intermediate in the n-butane oxidation and also, the next simplest C₄ hydrocarbon.

Explanation of Dissertation Format

This dissertation contains three papers, each written in a form suitable for publication in a technical journal. A general introduction has been included to allow the reader to understand the scientific and industrial relevance of this work. A reference list is provided at the end of each paper. A general summary and recommendations for future work are provided following the papers. References cited in the general introduction and general summary are listed at the end of dissertation. The research presented in each paper represents the original work conducted by the author.

PAPER I.
SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF
 ^{18}O -LABELED $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$

ABSTRACT

For the selective oxidation of n-butane to maleic anhydride, $(VO)_2P_2O_7$ has been identified as the most active and selective phase. However, the presence of various types of oxygen species made it difficult to understand the nature of the specific oxygen species involved in each of the intermediate steps. One solution to this problem is the isotopic reactive site-mapping approach. In this report, the feasibility of this approach has been investigated for $(VO)_2P_2O_7$ catalyst for n-butane conversion to maleic anhydride. A three-stage procedure was developed to synthesize a ^{18}O -labeled $(VO)_2P_2O_7$ catalyst. A judicious combination of infra red and Raman spectroscopical characterization of the catalyst, along with the *in situ* monitoring of the thermal reduction process used in the synthesis, allowed the determination of the location and the extent of ^{18}O -labeling in lattice oxygen sites. These results pointed to a very site specific ^{18}O -labeling. Preliminary activity testing studies showed that pulse reactor studies with this catalyst can be employed to investigate the redox mechanism in terms of specific surface layer oxygen sites.

INTRODUCTION

The chemical utilization of inert alkanes by converting them into valuable intermediates, is a relatively new and exciting area of heterogeneous catalysis. One of the few commercially successful industrial processes employing this type of chemistry is the selective oxidation of n-butane to maleic anhydride. The industrial catalyst for this process is a vanadium-phosphorus-oxide (V-P-O) catalyst. A wide variety of V-P-O phases have been investigated [1-11], but it is generally accepted that vanadyl pyrophosphate phase, $(VO)_2P_2O_7$, present in the industrial catalysts, is the most active and selective phase [6-12]. The structure, oxidation state and redox behavior of this catalyst has been widely investigated.

The conversion of n-butane to maleic anhydride involves the activation of paraffin, formation of a partially oxidized product having 8 hydrogen atoms removed and 3 oxygen atoms inserted. Several mechanisms have been proposed for this reaction [4-10]. A typical conversion pathway being: n-butane \rightarrow 1-butene \rightarrow 1,3-butadiene \rightarrow furan \rightarrow maleic anhydride. Though a numerous studies have addressed specific mechanistic aspects of this reaction, the catalytic sites involved in the selective as well as nonselective pathways have not yet been conclusively determined.

Based on n-butane oxidation studies over $(VO)_2P_2O_7$ catalyst at 400 C, Pepera and coworkers [13] proposed a Mars-van Krevelen mechanism in which the catalyst sequentially

underwent reduction and oxidation. It was believed that oxidation and reduction was limited only to near-surface regions. The stability of V^{4+} within the pyrophosphate structure was believed to be responsible for the limited oxidation capacity of the catalyst for C_4 hydrocarbon oxidation, in the absence of gas-phase oxygen, and for its resistance to bulk oxidation in the presence of excess oxygen at reaction temperatures. Surface V^{4+} was proposed to activate molecular oxygen and to be instrumental in the selective activation of the methylene C-H bonds in n-butane. V^{5+} surface centers were proposed to provide oxidative capacity to convert the activated hydrocarbon intermediates to products. The role of these V^{5+} species, however, remains controversial: Hodnett and Delmon attributed n-butane activation by Hodnett and Delmon [4].

Ebner and Gleaves [14] employed TAP reactor studies to determine the role of various oxygen species in the redox mechanism for C_4 hydrocarbon oxidation over $(VO)_2P_2O_7$. Their work indicated that both chemisorbed and surface layer oxygen participate in various stages of the redox mechanism. On the basis of the thermogravimetric experiments involving oxygen equilibrated $(VO)_2P_2O_7$, they demonstrated the formation of an irreversibly chemisorbed oxygen species on the catalyst by activated chemisorption of an electrophilic dioxygen molecule. The chemisorption was suggested to occur via a dissociative pathway on vanadium dimers. Results of TAP reactor studies with C_4 hydrocarbon reactant pulses, led these authors to suggest that two types of selective oxygen are present at the catalyst surface. A low concentration of irreversibly chemisorbed oxygen species was believed to be responsible for n-butane activation and the oxidation of furan to maleic anhydride. It was found to be present

in relatively low concentrations. The second type of oxygen species was believed to be a surface layer species. This species was used for intermediate oxidation steps, particularly in the allylic oxydehydrogenation of butenes and for oxygen insertion with ring closure to form furan. Centi and Trifiro [15], on the other hand, have postulated that $V^{5+}=O$ is responsible for oxygen insertion, and surface layer $V^{4+}=O$ or $V^{4+}-O-P$ sites are responsible for hydrogen abstraction.

Nature of the oxygen species involved in nonselective pathways has been the focus of number of studies. Based on the time resolved pulse studies of ^{18}O -cis-2-butene mixture, Ebner and Gleaves [14] identified two oxygen sources for the formation of CO_2 : (1) a "fast" source believed to be a highly reactive, chemisorbed oxygen which can react with hydrocarbon directly to form CO_2 ; and (2) a "slow" source attributed to surface layer oxygen. The exact chemical nature of this surface layer oxygen species was not determined. It is also not clear from the TAP studies whether irreversibly chemisorbed oxygen involved in n-butane activation is same as the oxygen involved in the fast route. Adsorbed dioxygen species have been proposed to be involved in CO_2 formation by Centi and coworkers [16], based on the blocking of oxygen adsorption sites by NH_3 . Nature of the different oxygen species and their exact role in the nonselective pathways is still not clearly understood.

Thus, significant contributions have been made in the understanding of the redox mechanism of n-butane conversion on $\beta-(VO)_2P_2O_7$. However, a number of discordances are present in the literature about the exact nature of the oxygen species involved in the individual steps. For example, it is established that surface layer oxygen are involved in ring

insertion reaction, however, the particular type of surface layer oxygen (viz. P-O-V, P-O-P, or V=O) that actually participates in this step is not conclusively determined. According to Haber and Serwicka [17], the reactivities of different types of surface layer oxygen sites depend upon the atoms bound to the oxygen. Several types of oxygen species exist at the surface of $(VO)_2P_2O_7$. Centi et al. [12] attributed the polyfunctional behavior of the catalyst, to the existence of these different types of oxygen species. Thus, without the knowledge of the reactivities of these oxygen species, a complete understanding of this redox system can not be achieved.

An investigation of the reactivity of individual type of oxygen will require some method of labeling these oxygen in the catalyst and later on monitoring their incorporation in the products using this label. Lashier and Schrader [18] have employed this principle to determine the reactivity of the lattice oxygen species in the oxidation of n-butane over β -VOPO₄. Using solid state procedures, they synthesized a β -VOPO₄ catalyst with ¹⁸O incorporated in specific lattice oxygen sites. The location and the extent of the ¹⁸O labeling was determined using laser Raman and infrared spectroscopies. The labeled catalyst was then pulsed with hydrocarbons, and the products were monitored for ¹⁸O incorporation by mass spectrometry. This work suggested that a partially dehydrogenated species react with P-O-V sites to produce a furan-like species. Further oxygen insertion at different P-O-V sites produces maleic anhydride. Furthermore, this work presented evidence for the additional routes to CO₂, in addition to the consecutive combustion of maleic anhydride.

To extend this approach to β -(VO)₂P₂O₇, one must first be able to synthesize a

^{18}O -labeled catalyst. Furthermore, this labeling has to be site specific, and the extent of incorporation in each site must be determined. Two routes have been well established for the synthesis of $(\text{VO})_2\text{P}_2\text{O}_7$ [19-20]: both of these are based on the reduction of V^{5+} compounds. The phosphate group may be added before or after the reduction. In the first route, initially a V^{5+} compound such as V_2O_5 or NH_4VO_3 is reduced and then reacted with *o*-phosphoric acid (*o*- H_3PO_4). The synthesis procedure can further differ in the type of the reducing medium used. The reducing media can be aqueous containing HCl or organic compound, most commonly isobutyl alcohol. In both the cases, vanadyl hydrogen phosphate hemihydrate is obtained, but the microstructure differs. Calcination at 450 C causes water loss which results in the formation of $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$. Typically, this phase is then activated by the reaction n-butane/air mixture at 400 C before it is used in reactor studies. The second route involves the solid state preparation of VOPO_4 , which is then reduced under nitrogen flow at 760 C. From the C_4 hydrocarbon oxidation activity studies of these catalysts, it is well established that $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ prepared by the organic route is the more active [21]. However, this route is generally preferred, it is not suitable for our ^{18}O -labeling technique: the presence of oxygen in the reducing media and the absence of a suitable step during which ^{18}O can be introduced in the catalyst make this route unsuitable. Same arguments are true for the aqueous synthesis route. Instead we have chosen a solid state preparation route which unavoidably leads to a slightly lower activity and selectivity [6]. The advantage of this approach is that the reversible redox between $(\text{VO})_2\text{P}_2\text{O}_7$ and VOPO_4 can be used to oxidize $(\text{VO})_2\text{P}_2\text{O}_7$ with ^{18}O to obtain a ^{18}O -labeled phase with a very specific incorporation of ^{18}O

into lattice oxygen sites [18]. This phase can be then reduced in an oxygen-free nitrogen stream back to produce ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ [19]. If the specificity of the ^{18}O -labeling observed in $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ is maintained after its reduction, a $(\text{VO})_2\text{P}_2\text{O}_7$ with ^{18}O -labeled in very specific lattice oxygen sites can be synthesized for use in studying the reactivity of surface layer oxygen.

In this study, we have synthesized a ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst using solid state techniques. Characterization of this catalyst by laser Raman and infrared spectroscopies, along with other complimentary techniques revealed that the labeling is highly site specific. Since it was established that the oxygen supply from this catalyst for C_4 hydrocarbon oxidation is limited, pulse reactor studies were best suited for conducting the mechanistic studies.

EXPERIMENTAL PROCEDURE

Synthesis of ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$

^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ was prepared using a three steps procedure. In the first step, $(\text{VO})_2\text{P}_2\text{O}_7$ (^{16}O , referred to as "unlabeled") was synthesized from the solid state reaction of $\text{NH}_4\text{H}_2\text{PO}_4$ with V_2O_5 using the procedure described previously by Moser and Schrader [6]. During the second step, this material was reacted with a stoichiometric quantity of $^{18}\text{O}_2$ to obtain $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$, as described by Lashier and Schrader [18]. In the final step, its conversion to ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ (referred to as "labeled") was achieved by high temperature reduction. This method is similar to that documented by Bordes [19]. 2 g of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ was spread in a platinum lined quartz boat and placed in a quartz tube (45-mm-i.d., 300-mm-long). The quartz tube was enclosed in a Lindberg programmable tube furnace. The quartz tube was purged with nitrogen (< 5 ppm oxygen, Matheson) for 3 h at room temperature. A nitrogen flow of 10 sccm was maintained during the following heat treatments. The furnace temperature was raised to 400 C in 2 h. After maintaining this temperature for 2 h, it was further raised to 760 C over 1 h period. This temperature was maintained for next 36 h before it was cooled down to 300 C at a rate of 50 C/min. The furnace power was then shut-off, and it was allowed to cool to room temperature. Surface areas of the final materials were 1.5 m²/g.

Catalyst Characterization

Bulk purity of phases formed during various stages of synthesis was examined using X-ray diffraction. Laser Raman and Fourier transform infrared spectroscopies were also used to further characterize the catalyst phases. Raman and infrared spectra of labeled catalyst phases showed band shifts/splitting due to the incorporation of the isotopic label. Thermal reduction of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ to labeled $(\text{VO})_2\text{P}_2\text{O}_7$ was characterized using *in situ* mass spectrometry to determine the ^{18}O stoichiometry in the catalyst.

Raman spectra were obtained with a Spex 1403 laser Raman spectrometer with the 514.3 nm line of a argon ion laser (Spectra Physics Model 2020-05). All spectra were recorded with 200 mW laser power at the source. A Nicolet 1180E computer system was used to accumulate 200 scans at a scanning speed of 6 cm^{-1}/s . and a resolution of 2 cm^{-1} . Peak intensities were integrated using a curve fitting routine available from Nicolet.

The infrared spectra were obtained using a Nicolet 60SX Fourier transform infrared spectrometer. Spectra were collected using KBr pellets containing 0.5-1 % of catalyst phases. A single spectrum represents accumulation of 256 scans at a resolution of 2 cm^{-1} .

The amount of ^{18}O in the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst was determined by characterizing the ^{18}O content of the oxygen evolved during the thermal reduction of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$. To accomplish this, a 2 g sample of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ was placed in 6-mm-o.d. quartz tube and connected to a vacuum system. The thermal reduction system consisted of the quartz tube containing catalyst to be reduced, an Ultratorr (Omaha Valves) high vacuum connector connected to a high vacuum valve which isolated a UTI 100C precision quadrupole mass

spectrometer and a 550 l/min turbomolecular pump. The mass spectrometer was controlled by a HP Vectra personal computer using Spectrasoft software from UTI. The tube was evacuated to less than 10^{-6} torr and held overnight. The quartz tube was then heated from ambient temperature to 400 C over a period of 3 h. After maintaining this temperature for next 2 h, it was further heated to 760 C over 1 h. The sample was held at this temperature until no additional oxygen could be detected leaving the sample. The amounts of $^{16}\text{O}_2$, $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ leaving the catalyst were determined with the mass spectrometer.

Catalyst Pretreatment

An *in situ* thermal pretreatment procedure was developed to achieve a clean surface of the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst, before it can be used in the mechanistic studies. After loading the reactor with catalyst, it was purged with helium flowing at 50 sccm for 3 h, at 40 C. The catalyst was then heated at a linear heating rate of 40 C/min to 760 C, and maintained at this temperature for 5 minutes. The catalyst was then allowed to cool back to reaction temperature at which it was maintained for 1 h. The reactor effluent was continuously monitored by a on-line mass spectrometer for water ($m/e = 18, 20$), oxygen ($m/e = 32, 34, 36$) and carbon dioxide ($m/e = 44, 46, 48$).

Reactor Studies and Mass Spectrometric Analysis

Reaction studies with n-butane and 1-butene with labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst were performed in a pulse flow micro-reactor system, shown in Figure 1. The micro-reactor was

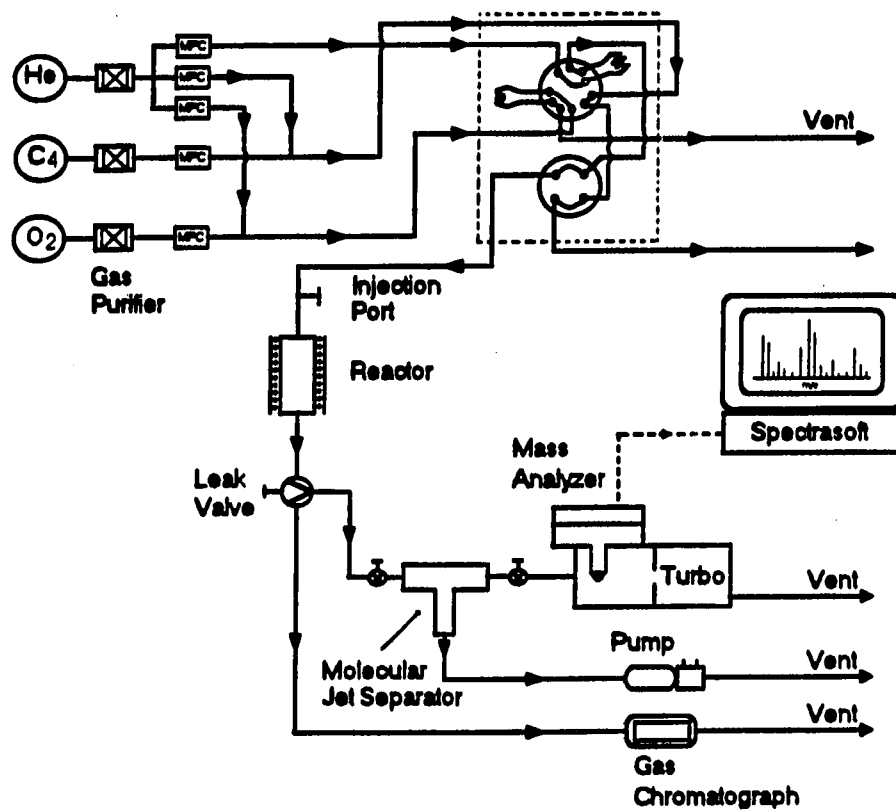


Figure 1: Pulse micro-reactor and analytical system

a passivated 1/4 in stainless steel tube. To achieve passivation, reactor was first treated with phosphoric acid (85%), followed by the calcination in oxygen at 550 C for 8 h. Catalyst bed was supported by quartz wool (Alltech) bobs, which were also treated using above procedure. About 0.3 g of catalyst was pelleted, crushed, and sieved to 10-20 mesh before use in each run. After loading the catalyst, it was thermally pretreated using the procedure developed earlier. After the pretreatment, catalysts were used at 500 C for n-butane and 450 C for 1-butene feeds. This temperature was maintained for 1 h before 100 consecutive pulses of C₄ hydrocarbon pulses were then introduced over the catalyst bed in the absence of the gas-phase oxygen. A 10-port Valco valve equipped with 0.5-ml injection loop for hydrocarbons, maintained at 125 C was used to pulse C₄ hydrocarbons. Gas compositions and flow rates of the gases fed to the injection loop and micro-reactor were controlled using Tylan mass flow controllers (Model FC260). n-Butane and 1-butene (Matheson, instrument grade) were diluted with helium (Air Products, zero grade) to a 6% molar hydrocarbon content. Residual oxygen from helium was removed using Oxy-trap (Alltech). Residual water was removed using molecular sieve/drierite gas purifiers (Alltech).

The reactor effluent was analyzed for the ¹⁸O content of the oxidation products using an on-line mass spectrometer. Mass spectrometry was performed using a UTI 100C precision quadruple mass analyzer controlled by a HP Vectra personal computer, which used Spectrasoft (UTI) software. The mass analyzer was interfaced with the micro-reactor system by a glass SGE (MJSS/ST) single stage molecular jet separator. The latter being used to increase the concentration of the products of interest by selectively stripping helium.

The amounts of ^{18}O in maleic anhydride (MAN), fuarn and carbon dioxide were determined for the oxidation of n-butane and 1-butene. For n-butane feed, methyl vinyl ketone was observed to form to considerable extent, and hence its ^{18}O content was also determined for n-butane studies. For 1-butene feed, phthalic anhydride (PAN) was formed during its reaction with the catalyst. However, its low yield did not allow to determine its ^{18}O content for these feeds. Because of the pulse nature of the experiments, it was not possible to accurately monitor the entire spectral region of interest ($m/e = 43-152$) for each pulse. Therefore, the mass spectrum was divided into 3 manageable groups which could be monitored, one group per pulse. These groups and the species of interest in them are noted in Table 1. To ensure that all the species are properly monitored, survey scans covering the entire spectral range were carried out using unlabeled catalyst. Any interferences at a m/e , due to other species present giving m/e peaks coincident with m/e peak of interest, were compensated using proper correction factors, and the corrected intensities were then used in the final calculations.

In this study, the level of ^{18}O in each species is expressed as a percentage of the total oxygen present in that species. Thus, the ^{18}O content of maleic anhydride was calculated as

$$\% ^{18}\text{O} = \frac{I_{100} + 2 \times I_{102} + 3 \times I_{104}}{3 \times (I_{98} + I_{100} + I_{102} + I_{104})} \times 100$$

In the case of 1-butene feed, phthalic anhydride formed caused interference at m/e 104 which was compensated by using reference at m/e 106. The level of ^{18}O incorporation in furan was calculated as

Table 1: Mass spectral groups, species of interest and interfering species

spectral group	m/e monitored	interfering species	interference at m/e	reference m/e ¹ for correction
maleic anhydride (MAN)	98, 100, 102, 104	-	-	-
furan, methyl vinyl ketone (MVK)	68,70 70,72	MVK furan- ¹⁸ O	70 70	69, 71 69, 71
carbon dioxide	44,46,48	n-butane 1-butene MAN	44 44, 48 44	42 42 45

1: these m/e were also monitored with the group to correct for the interference.

$$\% \text{ } ^{18}\text{O} = \frac{I_{70}}{(I_{68} + I_{70})} \times 100$$

For n-butane feed, methyl vinyl ketone was also formed and it gives a comparable signal at m/e 70. This necessitated correction of m/e 70 for furan and it was done using m/e 69 and 71 as references. This correction was also then used in the ¹⁸O content calculations for methyl vinyl ketone. For methyl vinyl ketone, the level of the ¹⁸O was calculated using following formula:

$$\% \text{ } ^{18}\text{O} = \frac{I_{72}}{(I_{70} + I_{72})} \times 100$$

Similarly, the amount of ^{18}O incorporated in CO_2 was determined as follow:

$$\% \text{ } ^{18}\text{O} = \frac{I_{46} + 2 \times I_{48}}{2 \times (I_{44} + I_{46} + I_{48})} \times 100$$

For n-butane feed, both n-butane and maleic anhydride contribute to m/e 44 and thus this m/e needed to be corrected. This was achieved by using m/e 42 and 45 as references, respectively. For 1-butene feed, interference due to 1-butene was at m/e 44 and 48, and was corrected using m/e 42.

EXPERIMENTAL RESULTS

Catalyst Synthesis and Characterization

Synthesis of labeled $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ was monitored by characterizing the phases formed by Raman and infra red spectroscopies. For the synthesis of unlabeled $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$, the nitrogen flow rate was found to be of crucial importance in order to produce a highly active catalyst. A nitrogen flow rate of 8 sccm was found to give an active, single phase $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ catalyst as determined by spectroscopical characterization. Characterization of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ formed in the second step, by Raman and infrared spectroscopies revealed band shifts due to the incorporation of ^{18}O into lattice oxygen sites, as reported earlier [18]. Amount of $^{18}\text{O}_2$ used in the solid state reaction and heat transfer were found to be the rate controlling parameters for this step. A 25% excess of $^{18}\text{O}_2$ over the stoichiometric amount was found to facilitate the complete conversion of $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ to $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$. Use of 25% excess of $^{18}\text{O}_2$ did not result in any "excess" incorporation of the labeled oxygen. Better heat transfer conditions were achieved by wrapping coils of stainless steel tubing around the reaction tubes.

The Raman and infrared spectra of labeled $(\text{VO})_2\text{P}_2\text{O}_7$ when compared to those of the unlabeled $(\text{VO})_2\text{P}_2\text{O}_7$, revealed spectral features which confirms a very specific incorporation of ^{18}O in the $(\text{VO})_2\text{P}_2\text{O}_7$ lattice. Raman band assignment has been discussed previously by Moser and Schrader [6], and will be followed in this work. The Raman spectra of labeled

and unlabeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalysts are compared in Figure 2. ^{18}O incorporation in the catalyst was evident from the Raman spectrum for labeled catalyst which showed a band at 908 cm^{-1} corresponding to the 923 cm^{-1} band for the unlabeled catalyst: this band was assigned to $\text{P}-^{18}\text{O}-\text{P}$ mode. Calculations based on the integration of the peak areas showed that about 30% of the $\text{P}-\text{O}-\text{P}$ oxygen is ^{18}O . Very weak intensities of the Raman bands assigned to $\text{V}=\text{O}$ (961 cm^{-1}) and PO_3 groups ($1010-1025$, $1128-1200\text{ cm}^{-1}$) did not allow an accurate quantitative determination of any isotopic labeling. The infrared spectrum was helpful in examining the ^{18}O in these sites.

FTIR spectra for labeled and unlabeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalysts are compared in Figure 3. The $\text{P}-\text{O}-\text{P}$ mode exhibited a similar shift in the infrared spectra: the 941 cm^{-1} peak for the unlabeled catalyst decreased in the intensity, and isotopically shifted peaks of nearly similar intensity appeared at 935 cm^{-1} and 919 cm^{-1} . The 923 cm^{-1} band for unlabeled catalyst, shifted to 903 cm^{-1} with its intensity reduced for isotopically labeled catalyst. A shoulder at 889 cm^{-1} may be due to the isotopic shift for 923 band. The 1061 cm^{-1} band assigned to PO_3 asymmetric stretches showed a shift to 1036 cm^{-1} with a shoulder at 1043 cm^{-1} , thereby revealing ^{18}O labeling at these sites. The 988 cm^{-1} band associated with the $\text{V}=\text{O}$ mode showed no indication of any isotopic labeling at this site. The characteristically broad band structure of the infrared spectrum makes quantitative analysis of the amount of ^{18}O present in different sites very difficult.

It was important to determine if any scrambling of ^{18}O occurred among various $\text{P}-\text{O}-\text{V}$ sites during the reduction of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ to labeled $(\text{VO})_2\text{P}_2\text{O}_7$. To investigate this

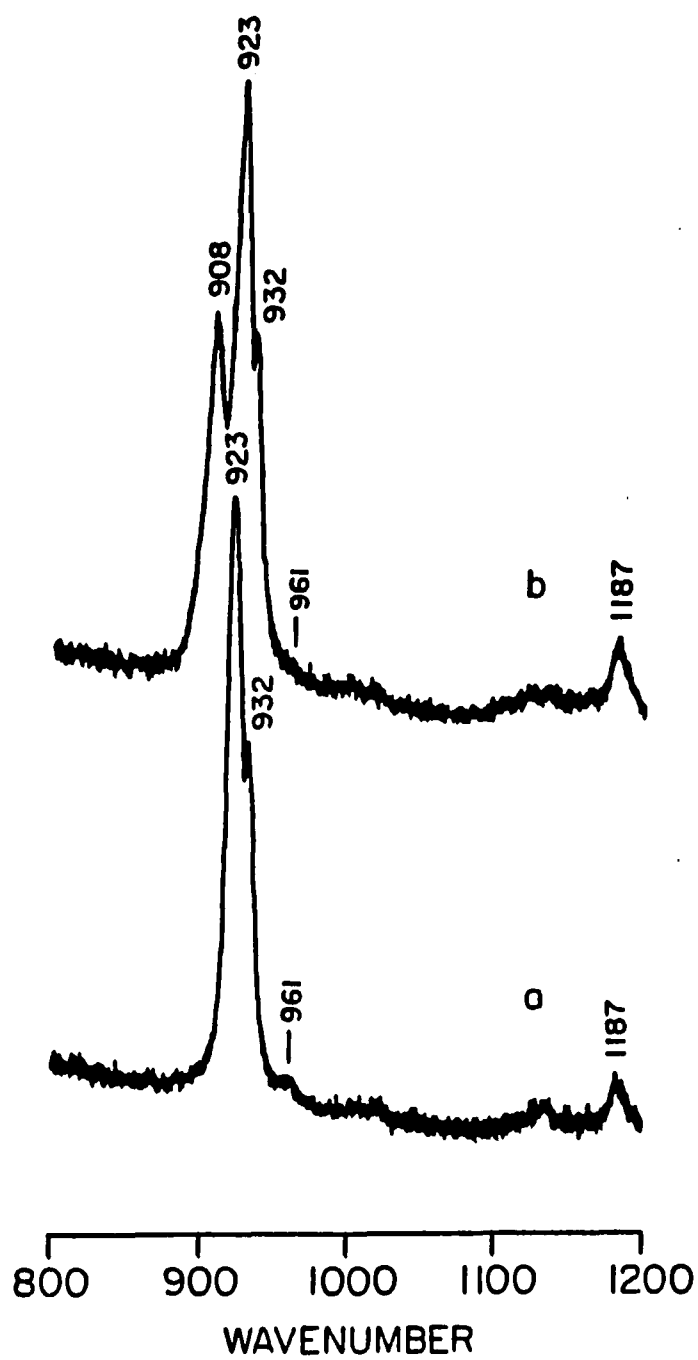


Figure 2: Laser Raman spectroscopic characterization of (a) labeled $(VO)_2P_2O_7$, and (b) unlabeled $(VO)_2P_2O_7$

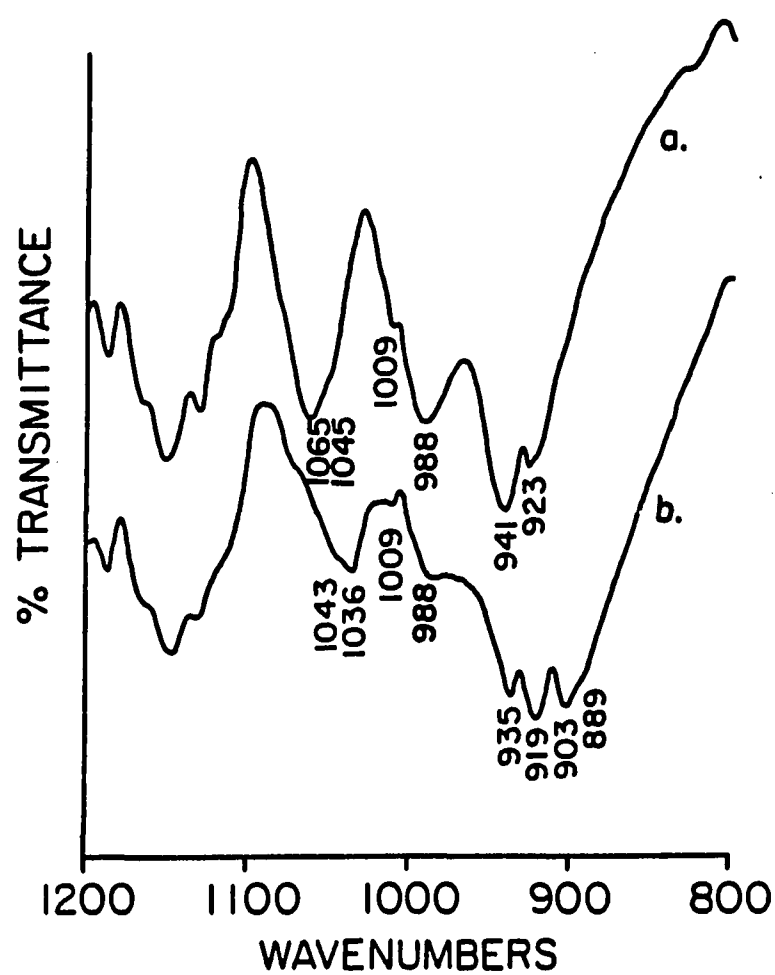


Figure 3: Fourier transform infra red spectroscopical characterization of (a) labeled $(VO)_2P_2O_7$, and (b) unlabeled $(VO)_2P_2O_7$

possibility, labeled $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ was reoxidized with stoichiometric amount of $^{16}\text{O}_2$. The Raman spectrum of this phase is given in Figure 4. The spectrum of the resulting material closely resembles labeled $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$, although some reduction in the extent of ^{18}O labeling in this material compared original $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ was observable. The specificity of the ^{18}O incorporation implied that no detectable ^{18}O "scrambling" among various P-O-V sites was observed. A particularly important feature of this reoxidation was that the intensity of P- ^{18}O -V band at 895 cm^{-1} decreased by greater percentage than that of the P- ^{18}O -V band at 985 cm^{-1} . This indicated that during the reduction of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ to labeled $(\text{VO})_2\text{P}_2\text{O}_7$, proportionately more ^{18}O was lost from the 895 cm^{-1} P- ^{18}O -V sites than the 985 cm^{-1} P- ^{18}O -V sites.

The information obtained from the Raman and infra red spectroscopic characterization of labeled $(\text{VO})_2\text{P}_2\text{O}_7$ is not sufficient to determine the amount ^{18}O remained in this catalyst. Hence, it was determined by *in situ* mass spectrometric monitoring oxygen ($m/e = 32, 34, 36$) leaving the catalyst during the thermal reduction of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ to labeled $(\text{VO})_2\text{P}_2\text{O}_7$. Almost all of the oxygen that leaves the catalyst was in the form of molecular oxygen, O_2 . The ^{18}O content of total oxygen leaving the catalyst was nearly 13-14% (almost entirely $^{18}\text{O}^{16}\text{O}$).

Catalyst Pretreatment

Results of monitoring the reactor effluent during the catalyst pretreatment are shown in Figure 5. For H_2^{16}O ($m/e = 18$), two large partly overlapping peaks were seen at

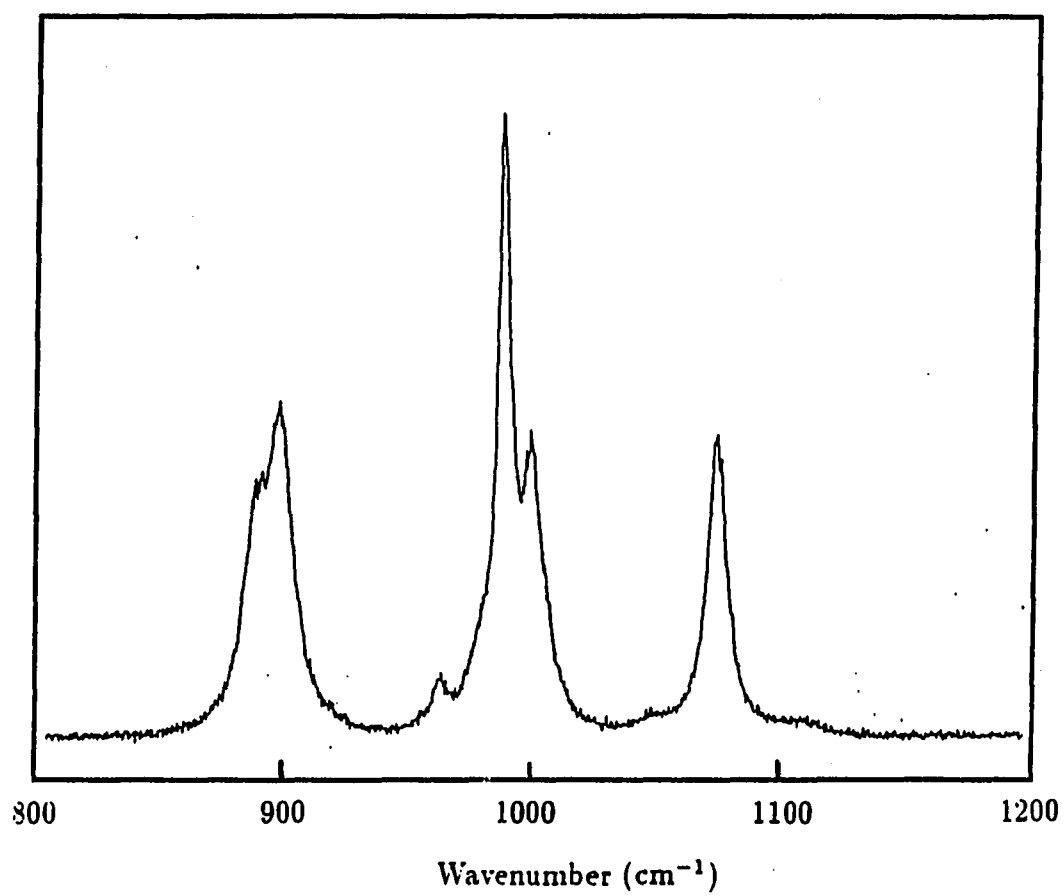


Figure 4: Laser Raman spectra of β -VOPO₄ obtained by oxidizing labeled (VO)₂P₂O₇ with stoichiometric amount of ¹⁶O₂

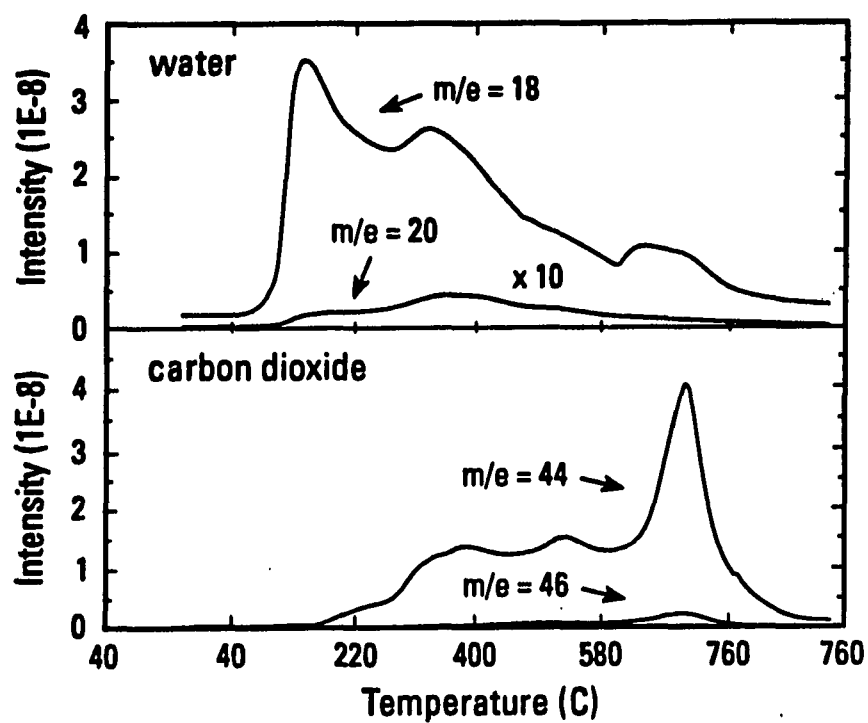


Figure 5: Mass spectrometry of the reactor effluent during the thermal pretreatment of the labeled $(VO)_2P_2O_7$ catalyst

130 C and 310 C. Two broad shoulder peaks were also seen at high temperatures of 510 C and 620 C. By 760 C, water desorption was complete. Calculations based on BET surface area and surface V-V ions density for $(VO)_2P_2O_7$, showed that amount of water that came out was approximately 0.3 monolayer. $^{16}O_2$ ($m/e = 32$, not shown) gave a straight baseline spectrum showing that it neither adsorbed on nor desorbed from the catalyst during the pretreatment. Three distinct peaks were seen for $C^{16}O_2$ ($m/e = 44$), two broad desorption peaks at 395 C and 540 C, and a large sharp one at 715 C. Like water, CO_2 desorption from the catalyst was complete by 760 C. Total amount of CO_2 that desorbed during the catalyst pretreatment was calculated to be roughly 0.25 monolayer.

Isotopically labeled water, $H_2^{18}O$ ($m/e = 20$) was observed in two small peaks that coincided with the first two peaks of $H_2^{16}O$. Total amount of $H_2^{18}O$ observed during pretreatment was less than 1% of that of the $H_2^{16}O$. No isotopically labeled oxygen ($m/e = 34, 36$) were seen. $C^{16}O^{18}O$ ($m/e = 46$) was seen only at high temperature with a broad peak at 715 C. $C^{18}O_2$ ($m/e = 48$) was not observed throughout the pretreatment. The area under $C^{16}O^{18}O$ desorption curve was about 2% of that of the $C^{16}O_2$.

Pulse Reactor Studies

(I) Anaerobic Oxidation of n-Butane over ^{18}O -Labeled $(VO)_2P_2O_7$

The results of anaerobic deactivation of ^{18}O -labeled $(VO)_2P_2O_7$ by n-butane pulses at 500 C are shown in Figure 6. It shows the trends in ^{18}O content of various oxygenated products for each n-butane pulse. For about first 60 pulses, ^{18}O content of maleic anhydride

showed a small variation around an average of about 8-8.5%. It started decreasing gradually after 60th pulse. However, it should be mentioned that signals for ^{18}O -enriched maleic anhydride ($m/e = 100, 102, 104$) became very weak after 60th pulse, which made it very difficult to integrate these peaks with high accuracy. This also explains the high degree of variability observed after 60th pulse for ^{18}O content. Throughout this experiment no ^{18}O incorporation was observed in furan as well as methyl vinyl ketone. Unlike these products, ^{18}O content of carbon dioxide showed a gradual decrease from its initial value of 4% to 0% by the end of the experiment.

(II) Anaerobic Oxidation of 1-Butene by ^{18}O -Labeled $(\text{VO})_2\text{P}_2\text{O}_7$

The results of anaerobic oxidation of 1-butene pulses by ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ at 450 C, are shown in Figure 7. Only furan and carbon dioxide were produced in substantial quantities during this experiment. Maleic anhydride was seen only during very first pulse. Phthalic anhydride was observed for first nine pulses. Yields of both of these products were negligibly low. No methyl vinyl ketone was detected throughout the experiment. For furan, a continuous decrease was observed from an initial value of about 17% to about 10% by 100th pulse. For carbon dioxide, the decrease in ^{18}O content was much more gradual; starting from 2% initially, by 100th pulse ^{18}O content dropped to about 0.5%.

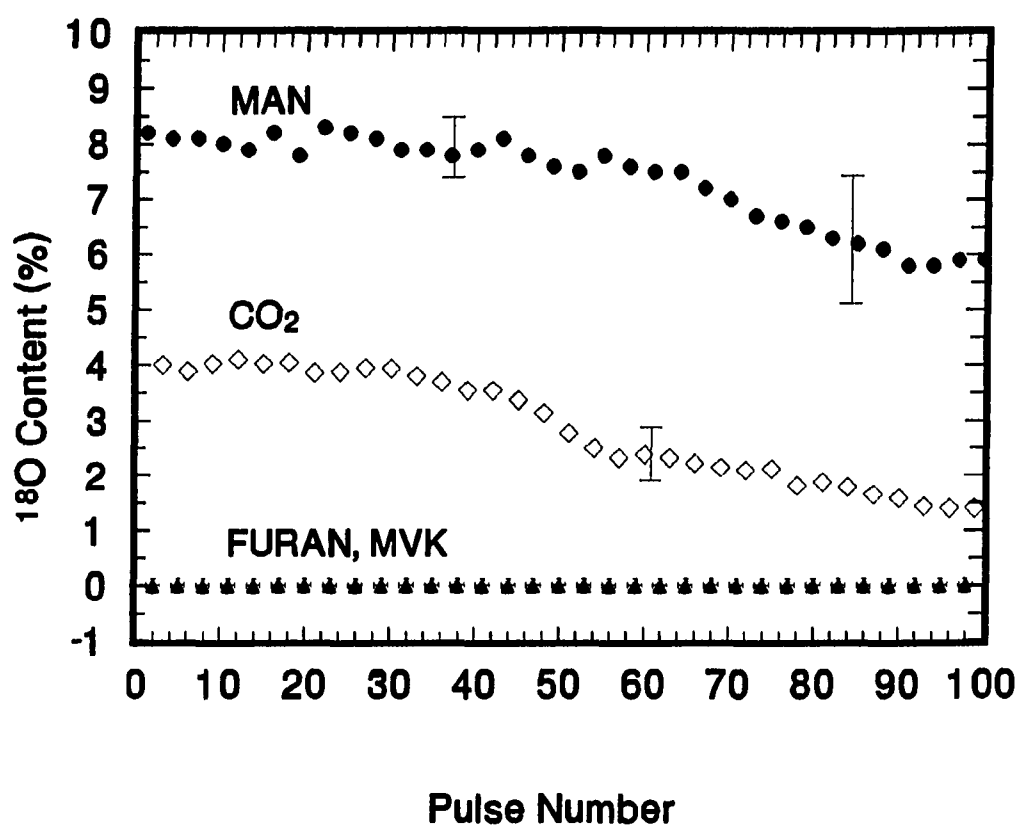


Figure 6: ^{18}O content of oxygenated products formed during the n-butane oxidation by labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst at 500 C

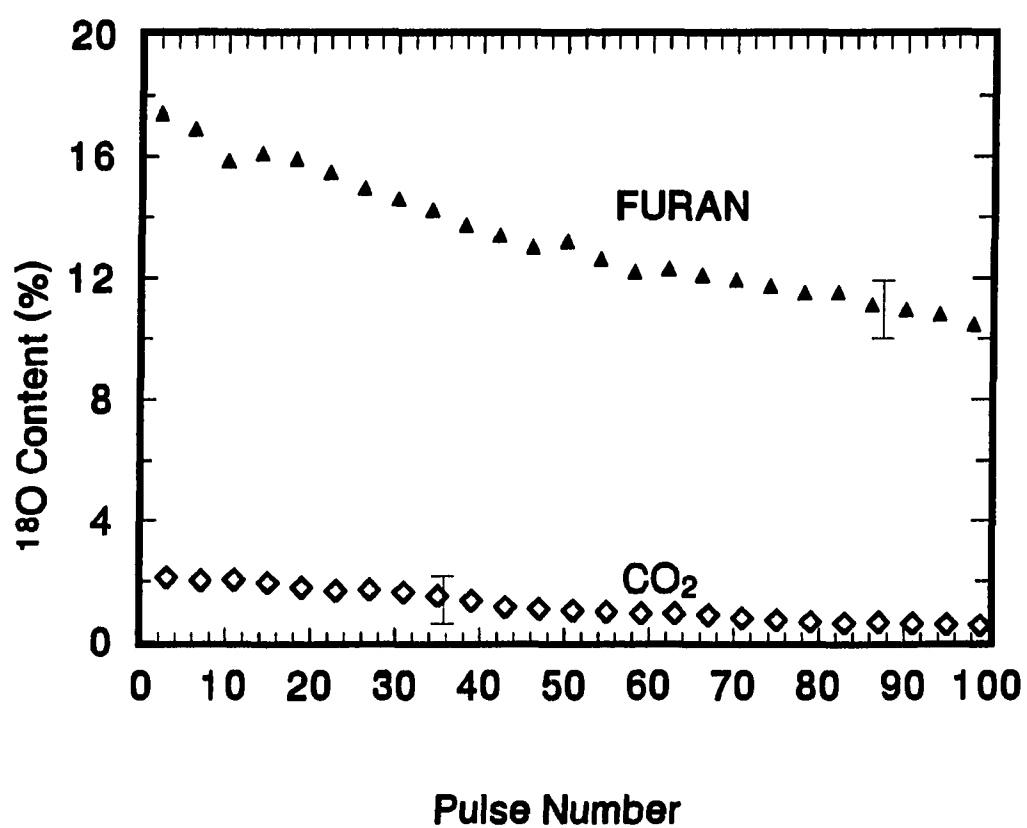


Figure 7: ^{18}O content of oxygenated products formed during the 1-butene oxidation by labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst at 450 C

DISCUSSION

Structure of $(VO)_2P_2O_7$

Previous investigations have clearly demonstrated that the activity and selectivity of V-P-O catalysts are strongly influenced by the method of preparation, surface P/V ratio, and crystal morphology [22]. Different synthesis routes also lead to different catalyst microstructure. Bordes and Courtine [23] have discussed these effects in terms of the different crystalline phases (β - and γ - $(VO)_2P_2O_7$), in which the former possess a network structure versus a layered structure for the γ - phase. According to these authors, β - $(VO)_2P_2O_7$ is formed either from β -VOPO₄ through a crystallographic shear mechanism or from the decomposition of vanadyl hydrogen phosphate under n-butane/air reaction mixture; γ - $(VO)_2P_2O_7$ forms by the dehydration of vanadyl hydrogen phosphate in air or reduction of γ -VOPO₄. However, the X-ray diffraction patterns for these phases are nearly identical, but it is not clear whether these phases have different structures [18]. Recent work by Ebner and Thompson [24] demonstrated that $(VO)_2P_2O_7$ can exist in at least two different crystal structures. These investigators were able to synthesize at least two different single crystals from the microcrystalline catalyst sample of $(VO)_2P_2O_7$ (originally prepared by the aqueous route), obtained from a fixed-bed reactor after more than 5000 hours of n-butane oxidation. These observations led to the suggestion that $(VO)_2P_2O_7$ is polymorphic and that the two crystal structures differ in the orientation of the vanadyl groups in adjacent chains. Of these

two structures, one is the already identified β -phase, while the other exhibits lattice parameters which are slightly dilated relative to β -(VO)₂P₂O₇.

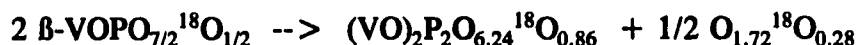
The synthesis route used in this study leads to the known β -(VO)₂P₂O₇ phase, and its structure is used as basis for the discussion in this work. The crystal structure of β -(VO)₂P₂O₇ is composed of distorted edge-sharing VO₆ octahedral pairs linked to corner-sharing pyrophosphate tetrahedra. A infinite chain structure is formed through V=O-V bonding. Pyrophosphate groups (P₂O₇) form two tridentate oxygen bridges with three separate chains, which gives rise to four P-O-V bonds, two V-O^P-V bonds and a P-O-P bond. Only equatorial oxygens in the VO₆ octahedral are shared with the pyrophosphate groups. As a result at least three crystallographically distinct P-O oxygen groups exist in this structure.

Incorporation and Location of ¹⁸O Sites

Thermal reduction of β -VOPO_{7/2}¹⁸O_{1/2} produced a site-specific labeled (VO)₂P₂O₇. The distribution of ¹⁸O in β -VOPO_{7/2}¹⁸O_{1/2} is known to be highly specific [18]. The PO₄ groups in β -VOPO₄ contain three crystallographically distinct P-O-V species. One of the P-O-V is enriched to 40% level, two of the four P-O-V are identical and contain about 5% ¹⁸O each while the fourth P-O-V contains no ¹⁸O as indicated in Figure 8. The V=O and V=O-V sites contain no ¹⁸O. This accounts for all of the ¹⁸O in β -VOPO_{7/2}¹⁸O_{1/2}. For labeled (VO)₂P₂O₇, Raman and infrared characterization indicated no ¹⁸O labeling at V=O sites. Calculations based on the integration of the areas of 908 cm⁻¹ (P-¹⁸O-P) and 923 cm⁻¹ (P-¹⁶O-P) bands showed that about 30% of the P-O-P oxygen is ¹⁸O. The labeling of this

site was further confirmed by the FTIR spectra. FTIR spectra also showed that the P-O (PO_3) sites which form the tridentate bridges are enriched in ^{18}O . However, the broad structure of this infrared band did not allow an accurate estimate of the extent of this enrichment.

The extent of ^{18}O enrichment in various P-O-V sites were not readily available from the spectral data. Therefore, the amount of ^{18}O in the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst was determined by the stoichiometric measurements of ^{18}O oxygen released during the reduction process. ^{18}O content of the original $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ is 10%. The *in situ* mass spectral monitoring of the thermal reduction of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ to ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ revealed that ^{18}O content of the total oxygen released during this reduction is about 14%. By ^{18}O balance, this results in an overall 9% ^{18}O content for labeled $(\text{VO})_2\text{P}_2\text{O}_7$. Since, the infrared spectra indicated that no ^{18}O appeared in V=O sites, all the ^{18}O is in the pyrophosphate groups. The ^{18}O content of the pyrophosphate groups must be therefore about 12%. Since about 30% of the P-O-P oxygen is ^{18}O , again by ^{18}O balance, the remaining PO_3 (i.e. P-O-V) sites contain about 9% ^{18}O . The stoichiometry of the reduction therefore can be written as:



A pyrophosphate (P_2O_7) group is formed by the condensation of two PO_4 groups while one of the eight oxygen is removed during the reduction. Reoxidation of labeled $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ with ^{16}O indicated that no scrambling of ^{18}O among the various P-O-V sites occurs, and that all the P-O-V sites maintain their integrity throughout redox cycles. Furthermore, the amount of ^{18}O oxygen lost from the 5% labeled P-O-V sites is higher than

Site	^{18}O content (%)	Raman band (cm^{-1})
P-O-V (E_1)	40	896
P-O-V (E_2)	5	987
P-O-V (B)	0	1072
V=O-V	0	998

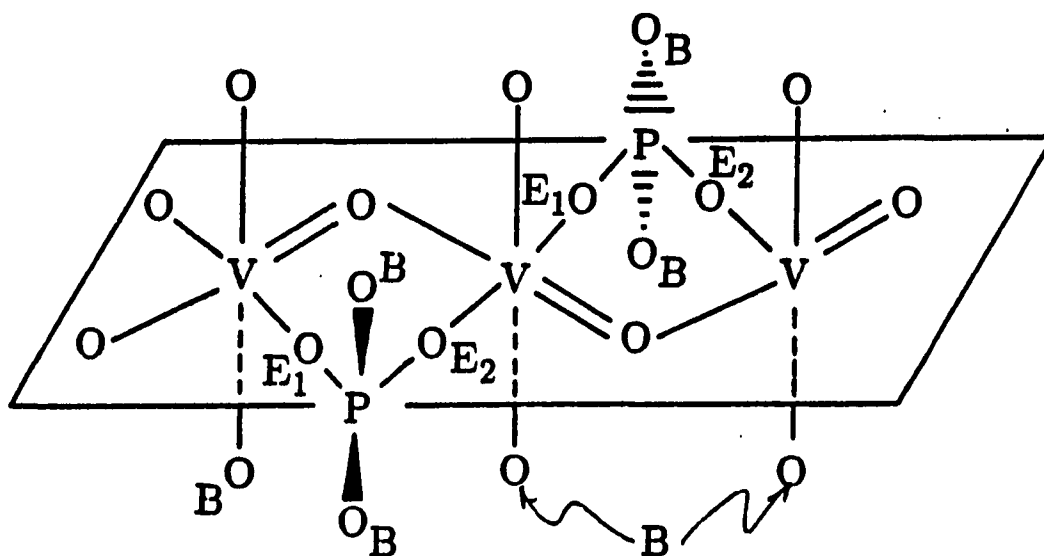


Figure 8: Distribution of ^{18}O in $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$ [18]

from the 40% labeled P-O-V sites. Based on this information, along with the knowledge of the ^{18}O labeling in $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$, and the ^{18}O content of $(\text{VO})_2\text{P}_2\text{O}_7$, ^{18}O distribution in the various sites of labeled $(\text{VO})_2\text{P}_2\text{O}_7$ was determined by taking ^{18}O balance. According to these calculations, 25% of the oxygen removed in the thermal reduction must be from the 40% P-O-V sites in $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$, while the remaining 75% is from the 5% P-O-V sites. For the P-O-P sites, 25% oxygen originates in the 5% P-O-V site of $\beta\text{-VOPO}_{7/2}^{18}\text{O}_{1/2}$, while the rest comes from the 40% P-O-V site. The remaining 5% and 40% P-O-V sites occupy tridentate bridging P-O-V sites in $(\text{VO})_2\text{P}_2\text{O}_7$.

Thus, the result is a $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst with specifically labeled P-O sites. In the context of the bulk $(\text{VO})_2\text{P}_2\text{O}_7$ structure, the spectroscopic and thermal reduction data suggest that the two unlabeled P-O sites are the two V-O^P-V groups present in each pyrophosphate group, while the four P-O-V groups are the labeled sites, in addition to the P-O-P sites labeled at the 30% level. The distribution of ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ in [020] plane of the bulk structure is shown in Figure 9.

Thermal Pretreatment

Labeled $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ catalyst so prepared will be used in studies which involve determining ^{18}O content of various oxygenated products. However, V-P-O phases are known to be mildly hygroscopic; they are also known to pick up carbon dioxide when exposed to air [25]. During the loading of the reactor, the catalyst is exposed to air for a considerable time (5-8 minutes). This may lead to a catalyst surface covered with water and carbon

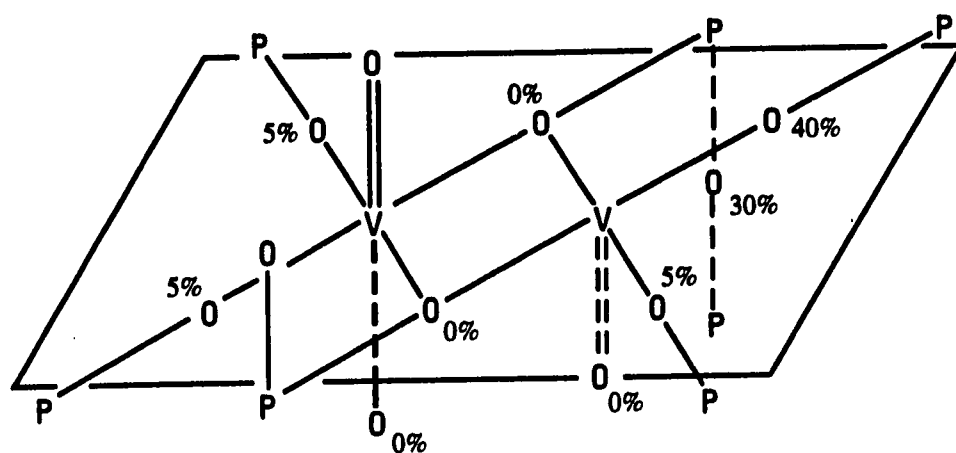


Figure 9: Distribution of ^{18}O in the labeled $(\text{VO})_2\text{P}_2\text{O}_7$

dioxide. Presence of water in the C₄ hydrocarbon feeds is known to affect this reaction considerably [25]. Similarly, oxygen from water and carbon dioxide can exchange with that of the catalyst, resulting in some ¹⁸O loss from the catalyst surface. An efficient way of getting a clean surface is thermal desorption. It is particularly suitable for this system since it is an *in situ* technique. The large amounts of water and carbon dioxide seen desorbing from the catalyst surface during the pretreatment clearly shows the very need for such treatment. However, the loss of ¹⁸O during the pretreatment was insignificant, and thus any recalculation of ¹⁸O content of catalyst surface sites was not required.

Pulse Reactor Studies

The major objective for this synthesis and characterization of a labeled (VO)₂P₂O₇ catalyst was to conduct isotopic reactive-site mapping (IR-SM) studies. The IR-SM approach to study the reactivities of the oxygen sites of a ¹⁸O-labeled catalyst involves comparing the ¹⁸O incorporation in the various oxygenated products of the anaerobic oxidation with the levels of ¹⁸O labeling observed in the lattice oxygen sites. In an earlier study [18, 26], where this approach was developed using a labeled β-VOPO₄, both continuous flow and pulse modes of operation were successfully used to carry out the reactor studies. Under anaerobic conditions, both n-butane and 1-butene feeds reduced this catalyst extensively. Furthermore, the ¹⁸O levels in their products were nearly constant throughout these studies. The results of the studies with labeled (VO)₂P₂O₇ catalyst differed sharply as compared to that with labeled β-VOPO₄ catalyst. The ¹⁸O levels in the oxygenated products of both, n-butane and 1-butene,

over labeled $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ were not constant, but rather a gradual decrease occurred with successive pulses. These studies suggest that $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$ has a basically different mechanism for replenishing reduced surface sites with bulk oxygen: clearly, catalyst has only a very limited amount of lattice oxygen available for C_4 oxidation. Consequently, adsorbed and surface layer oxygen can be expected to play important roles in the catalytic mechanism, along with some degree of participation by bulk oxygen may be involved. Whereas surface layer oxygen reacts directly with the hydrocarbon, bulk oxygen can participate only by replenishing the reduced surface layer sites. It is this ability of bulk oxygen to replenish, which determines the extent to which catalyst can be reduced under anaerobic conditions. For $(\text{VO})_2\text{P}_2\text{O}_7$, the catalyst activity in the absence of gas-phase oxygen will be short-lived. It is therefore clear that pulse reactor studies are more suited to determine the reactivity of oxygen sites as well as the extent to which these sites are available.

The level of ^{18}O in the products, was seen to differ considerably depending upon the feed. No incorporation of ^{18}O was observed in furan during n-butane oxidation, however, ^{18}O content of furan formed during 1-butene oxidation, gradually decreased from initial 16% value. The ring oxygen of furan in the n-butane oxidation must come from a surface layer oxygen site which is not labeled with ^{18}O . We attribute this oxygen to unlabeled $\text{V-O}^{\text{P-V}}$. On the other hand, for furan produced during the 1-butene oxidation, this oxygen is supplied by a site whose ^{18}O content is about 14-17%. This would probably result from a combination of P-O-V sites, but perhaps excluding the $\text{V-O}^{\text{P-V}}$ site. Thus, different reactive sites seem to be involved in same elementary step (in this case, the oxygen insertion to form furan) for

different hydrocarbon feeds. Such difference would however, imply that the initial interaction of these feeds with the catalyst surface must be fundamentally different.

Another important implication of differences in ^{18}O -levels in a product for two C_4 hydrocarbon feeds is that, a surface layer site seems to have different roles in different hydrocarbon oxidation. Rather as demonstrated elsewhere [27], the availability as well as the selectivity of these reactive sites is dependent on the hydrocarbon feed. Numerous studies have employed olefin intermediates (1-butene, 1,3-butadiene) to study the mechanism of n-butane oxidation. However, it is clear from these IR-SM studies that although the adsorbed species formed are likely to be partially dehydrogenated and even "olefin-like", since they are strongly chemisorbed, makes their interaction with the catalyst surface very different than that of gas-phase "free" species. As a result, the inferences drawn about the mechanism of n-butane oxidation using the studies with known intermediates over this catalyst may not be valid. To great extent, this explains the discordances seen in the literature about the nature of the active oxygen involved in n-butane oxidation over $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst.

CONCLUSIONS

A ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst was synthesized by a three step procedure based on the solid state reaction techniques. The location and extent of ^{18}O sites was determined using a combination of spectroscopical characterization tools such as infra red and Raman spectroscopies. The ^{18}O labeling of lattice oxygen sites was found to be very specific.

Preliminary anaerobic C_4 hydrocarbon pulse reaction studies with labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst showed that this catalyst can be employed in an isotopic reactive-site mapping (IR-SM) studies. These studies allow to determine the reactivity of individual surface layer oxygen sites for C_4 hydrocarbon oxidation. These studies also indicated that the initial interaction of n-butane with $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst surface is fundamentally different as compared to that of 1-butene. Furthermore, the reactivity of a particular type of surface layer oxygen seems to depend upon the hydrocarbon feed.

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PAPER II.

**SELECTIVE OXIDATION OF C₄ HYDROCARBONS OVER ¹⁸O-LABELED
B-(VO)₂P₂O₇: IDENTIFICATION OF THE REACTIVE SITES BY
PULSE REACTOR STUDIES**

ABSTRACT

Role of the surface layer oxygen and the participation of bulk oxygen in the catalytic oxidation of n-butane to maleic anhydride was studied using a modified isotopic reactive-site mapping (IR-SM) technique. β -(VO)₂P₂O₇ catalyst used for these studies was labeled with ¹⁸O into specific lattice oxygen sites. Pulse micro-reactor studies were conducted to anaerobically oxidize n-butane and 1-butene by the labeled catalyst. Mass spectrometry of the oxidation products allowed to determine the level of ¹⁸O incorporation in these products. A comparison between the ¹⁸O content in products to those in the various catalyst lattice sites, allowed to associate specific surface layer sites with the specific mechanistic steps for both selective and nonselective pathways. Participation of bulk oxygen in redox mechanism was found to be limited, with redox mechanism involving only the surface monolayer. These studies also indicated that the selectivity of different sites depend on the reactivity of hydrocarbon feeds, and therefore the initial interaction of the paraffin vs. olefin feeds with the catalyst surface are fundamentally different.

INTRODUCTION

Selective oxidation reactions are widely employed in the petrochemical industry to convert relatively inert hydrocarbons into valuable reactive intermediates. Since, this is achieved by introducing a functional group (viz. -CHO, -CO) in the reactant molecule, it is also referred as the functionalization of hydrocarbons [1]. Due to their inert nature, functionalization of alkanes have not been commercially feasible. Rather, the conversion of n-butane to maleic anhydride is one of the few industrial processes employing this type of chemistry. Typically, all these reactions utilize highly selective catalysts which enhance the rate of selective pathways, while inhibiting the nonselective pathways. At the heart of a catalyst are the reactive sites which bring out the chemical transformations that lead to selective products. Therefore, any fundamental understanding of mechanism for a catalytic reaction requires an understanding of the nature of these active sites.

Oxidation of n-butane to maleic anhydride is a 14 electron process which involves the paraffin activation, stabilization of reactive intermediates, removal of 8 hydrogen atoms, and the insertion of 3 oxygen atoms. Several mechanisms, ranging from a very simple one to the highly complicated ones, involving surface or free olefins and oxygenated products have been proposed for this reaction [2-5]. Thus, the catalyst for this reaction has to be a polyfunctional catalyst capable of accomplishing different functions involving different types of active sites [6]. For the conversion of n-butane to maleic anhydride, vanadyl pyrophosphate, $(VO)_2P_2O_7$,

has been identified as the most active and selective of the V-P-O phase [7-10]. The industrial catalysts are much more complex, however, are known to contain $(VO)_2P_2O_7$ phase. Thus, this phase has been employed in numerous investigations.

A reduction-oxidation (redox) mechanism has been established for this reaction [11]. The focus of the recent work in this area is thus to determining the functions of various oxygen species (present in this catalyst system), in each of the primary reaction steps in redox mechanism. Pepera et al. [11] have studied the nature of the active sites for n-butane oxidation over the $(VO)_2P_2O_7$ catalyst at 400 C. Based on their kinetic and oxygen chemisorption studies, these investigators proposed V^{4+} sites on the catalyst surface to be instrumental in the selective activation of C-H bond in n-butane. Furthermore, V^{5+} sites on the catalyst surface were proposed to provide the additional oxidative capacity for further conversion of activated n-butane to selective products.

Role of various oxygen species in the n-butane conversion was also studied by Ebner and Gleaves [12] using a TAP (temporal analysis of products) system. They proposed a highly mobil-yet irreversibly adsorbed-oxygen species to be responsible for n-butane activation and the oxidation of furan to maleic anhydride. This oxygen species was shown to be formed by strong chemisorption of an electrophilic dioxygen molecule at a V^{4+} site. Surface layer oxygen was proposed to be involved in the intermediate steps, specifically allylic oxydehydrogenation and oxygen insertion leading to ring closure to form furan. Two sources of oxygen were identified for CO_2 formation: a "fast" one being the highly reactive short-lived chemisorbed oxygen, and the other "slow" being the surface layer oxygen. In

general, these studies have contributed to a better understanding of the redox mechanism. However, there are many discordances in this literature. For instance, the exact nature of the surface layer sites involved in specific intermediate steps is not yet conclusively determined.

Lashier and Schrader [13] have studied the reactivity of the surface layer oxygen sites of β -VOPO₄ by specifically labeling some of the lattice oxygen sites by ¹⁸O. The location and the extent of ¹⁸O incorporation was determined by infrared and Raman spectroscopical characterization. These sites were then identified as either the selective or nonselective based on the results of monitoring the ¹⁸O incorporation into the products of selective oxidation of C₄ hydrocarbons over this labeled catalyst.

In a previous investigation [14], we developed the synthesis of a (VO)₂P₂O₇ catalyst with ¹⁸O labeled in very specific lattice oxygen sites. In this study, we have used this catalyst to extend the isotopic reactive-site mapping (IR-SM) approach, to study the surface reactive sites of the (VO)₂P₂O₇ catalyst. Another area of discordances in n-butane oxidation has been the role of the bulk oxygen in the redox mechanism. Particularly, the availability of the reactive sites i.e., the extent to which these surface layer sites are replenished by the bulk oxygen is not clearly understood [11, 15, 16]. Though recent investigations point to a redox mechanism limited to near surface layers, no quantitative investigations have been carried out. In this work, we have modified the IR-SM technique to make it quantitative so as to study the availability of various sites. This work has provided new information regarding the role of specific surface layer oxygen sites in the reaction pathways and their availability.

EXPERIMENTAL PROCEDURE

Catalyst

A ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ (referred as to "labeled") catalyst was used for these studies. It was synthesized by the three step procedure reported earlier [14]. The purity and the consistency of this catalyst was examined using laser Raman and infrared spectroscopies.

Pulse Reactor Studies

Reaction studies of n-butane and 1-butene with the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst were carried out in a pulse-reactor system, a schematic of which is presented in Figure 1. The reactor was constructed from a passivated 1/4 in stainless steel tube. The passivation was achieved by first treating reactor with phosphoric acid (85%) and then calcining in oxygen at 550 C for 8 h. Quartz wool (Alltech) used for supporting the catalyst bed was also treated using above procedure. For each experiment, 0.2 g of catalyst was pelleted, crushed, and sieved to 10-20 mesh before use. After loading the catalyst, it was thermally pretreated as following: the reactor was purged with helium flowing at 50 sccm for next 3 h at 40 C, and then was heated to 760 C at a heating rate of 40 C/min. This treatment was developed earlier [14]. It was held at this temperature for 5 min and then allowed to cool back to reaction temperature (500 C for n-butane and 450 C for 1-butene feeds). This temperature was maintained for next 1 h. Reactant pulses were then introduced in the desired fashion.

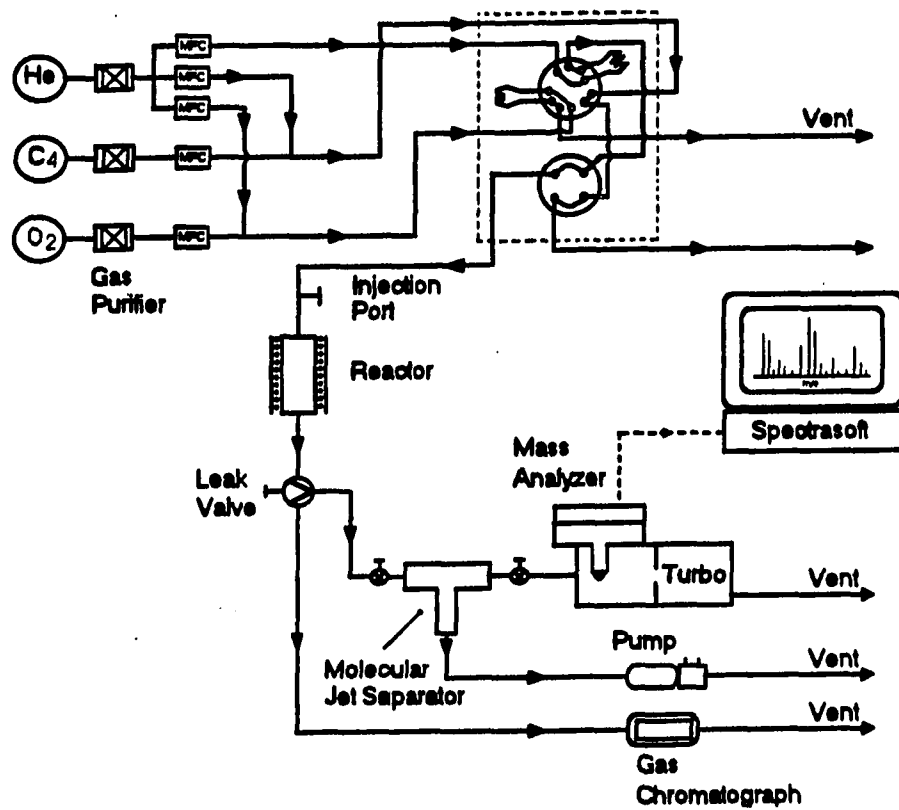


Figure 1: Pulse micro-reactor and mass spectrometric analytical system

The system for pulsing consisted of 10-port Valco valve equipped with 0.5-ml injection loop for hydrocarbon and 0.2-ml for oxygen. The valve assembly containing the injection loops was maintained at 125 C. Tylan mass flow controllers (Model FC260) were used to regulate the gas compositions and flow rates of the gases fed to the injection loop and the micro-reactor. n-Butane and 1-butene (Matheson, instrument grade) were diluted with helium (Air Products, zero grade) to a 6% molar hydrocarbon content. Residual oxygen from these gases was removed using Oxy-trap (Alltech).

To determine the reactivity and the extent of availability of various surface layer oxygen sites for the C₄ hydrocarbon oxidation, hydrocarbon (n-butane, 1-butene) pulses were introduced on the catalyst under anaerobic conditions at a rate of 1 pulse per minute. Pulsing was continued till no further conversion of C₄ hydrocarbon was observed. The reactor effluent was analyzed for the yields of various products and their ¹⁸O content.

Alternate hydrocarbon-oxygen pulse studies were also conducted. For these studies, oxygen (Air Products, 99.8 %) was diluted with helium to give a 21 % molar concentration. The hydrocarbon concentration was maintained at 6 % by diluting it with helium in appropriate proportions. Experiment started with a hydrocarbon pulse and continued with alternate oxygen/hydrocarbon pulses. Oxygen was pulsed 15 seconds before each hydrocarbon pulse. 45 s after the hydrocarbon pulse, next oxygen pulse was introduced.

The consecutive pulses of C₄ hydrocarbons can lead to the formation of carbonaceous deposits on the catalyst surface, which can lead to a reduced catalyst activity. To investigate this possibility, two experiments were carried out with n-butane feed at 500 C. In each of

these experiments, initially 0.2 g of catalyst was loaded in a reactor and thermally pretreated as described earlier. In the first experiment, the catalyst was pulsed with a single n-butane (6% in He) pulse followed by a number of oxygen pulses. Carbon dioxide evolved during the oxygen pulses was determined by mass spectrometry. In the next experiment, the catalyst was pulsed with 100 consecutive n-butane pulses. The catalyst was then pulsed with oxygen (21% in He) till no additional carbon dioxide was observed to form. To ensure that all carbonaceous materials are converted to carbon dioxide, the temperature of the catalyst was raised to 700 C during the oxygen pulses.

Finally, oxygen chemisorption was studied by dynamic adsorption technique at 450 C for the labeled catalyst. 0.2 g of the labeled catalyst was loaded in the reactor and then thermally pretreated, to achieve a clean surface. After cooling the catalyst to 450 C and maintaining this temperature for next 1 h, the catalyst was pulsed with oxygen (10% in He) at a rate of 1 pulse per minute. Pulsing was continued till, further oxygen pulses did not result in any additional chemisorption. The process was monitored by mass spectrometry.

Mass Spectrometric Analysis

The product analysis was carried out using a on-line mass spectrometer. A UTI 100C precision quadrupole mass analyzer controlled by a HP Vectra personal computer using Spectrasoft (UTI) software was used. The mass analyzer was interfaced with the reactor system by a glass SGE single stage molecular jet separator (MJSS/ST).

Because of the pulse nature of the experiments, it was not possible to accurately

monitor the entire spectral region of interest ($m/e = 43-106$) for each pulse. Therefore, the mass spectrum was divided into 3 manageable groups which could be monitored, one group per pulse. These groups and the species of interest in them are noted in Table 1. Survey scans covering the entire spectral range were made using unlabeled catalyst to ensure that all the species were accounted for. Most often, fragments from one species present gave m/e peaks coincident with m/e peaks from other species. This necessitated use of the correction factors for that m/e based on another m/e of the interfering species. These factors were determined by studying the fragmentation patterns of both reactants and products, fed individually or as a mixture, with or without unlabeled catalyst under reaction conditions. The results of these studies were used in deciding which m/e should be monitored in each group, and compensating for the interfering species. The corrected intensities were then used in the final calculations. The amounts of ^{18}O in maleic anhydride (MAN), fumaric acid and carbon dioxide were determined for the oxidation of n-butane and 1-butene. For n-butane feed, methyl vinyl ketone (MVK) was observed to form to considerable extent, and hence its ^{18}O content was also determined for n-butane studies. For 1-butene feed, phthalic anhydride (PAN) was formed during its reaction with the catalyst. However, its low yield did not allow to determine its ^{18}O content for these feeds.

The level of ^{18}O in each species is expressed as a percentage of the total oxygen present in that species. Thus, for maleic anhydride, the ^{18}O content was calculated as

$$\% \text{ } ^{18}\text{O} = \frac{I_{100} + 2 \times I_{102} + 3 \times I_{104}}{3 \times (I_{98} + I_{100} + I_{102} + I_{104})} \times 100$$

Table 1: Mass spectral groups, species of interest and interfering species

spectral group	m/e monitored	interfering species	interference at m/e	reference m/e ¹ for correction
maleic anhydride (MAN)	98, 100, 102, 104	-	-	-
furans, methyl vinyl ketone (MVK)	68,70 70,72	MVK furan- ¹⁸ O	70 70	69, 71 69, 71
carbon dioxide	44,46,48	n-butane 1-butene MAN	44 44, 48 44	42 42 45

1: these m/e were also monitored with the group to correct for the interference.

For 1-butene feed, phthalic anhydride formed caused interference at m/e 104 which was compensated using reference m/e 106. The ¹⁸O content in furan was calculated as

$$\% \text{ } ^{18}\text{O} = \frac{I_{70}}{(I_{68} + I_{70})} \times 100$$

For n-butane feed, methyl vinyl ketone was also formed and it gives a comparable signal at m/e 70. This necessitated correction of m/e 70 for furan and was done using m/e 69 and 71. Similarly, the ¹⁸O content of methyl vinyl ketone was calculated using following formula:

$$\% \text{ }^{18}\text{O} = \frac{I_{72}}{(I_{70} + I_{72})} \times 100$$

For n-butane feed, both n-butane and maleic anhydride contribute to m/e 44, and this m/e needed to be corrected for CO₂ (m/e 44). This was achieved by using m/e 42 and 45 as references, respectively. For 1-butene feed, interference due to 1-butene at m/e 44 and 48, were corrected using m/e 42. The ¹⁸O content of CO₂ was determined as follow:

$$\% \text{ }^{18}\text{O} = \frac{I_{46} + 2 \times I_{48}}{2 \times (I_{44} + I_{46} + I_{48})} \times 100$$

The mass spectrometer was calibrated to measure the actual amounts of C₄-hydrocarbons (n-butane, 1-butene and 1,3-butadiene), and oxygenated products (maleic anhydride, furan, methyl vinyl ketone and carbon dioxide). This was achieved by pulsing the known amounts of these hydrocarbons as standard mixtures as well as individual samples, while monitoring the appropriated m/e signals. These signals were then correlated with the amount of hydrocarbon in the pulse. To provide low concentrations of furan (Kodak) and maleic anhydride (Kodak), helium was fed through a saturator [17] maintained at a temperature which will provide a vapor pressure less than 10 torr for that particular species. For maleic anhydride, thus, the saturator was maintained at 67 C, providing a feed of slightly less than 1% mol maleic anhydride. For furan, the saturator was a dewar flask which contained a dry ice/acetone bath. The system was maintained at -78 C, thereby providing a furan vapor pressure of about 1 torr or about 0.1% mol.

EXPERIMENTAL RESULTS

Anaerobic Oxidation of n-Butane over the Labeled $(VO)_2P_2O_7$

The results of anaerobic deactivation of the labeled $(VO)_2P_2O_7$ by n-butane pulses at 500 C are shown in Figures 2 and 3. Figure 2 shows the trends in ^{18}O content of various oxygenated products for each n-butane pulse. For about first 60 pulses, ^{18}O content of maleic anhydride showed a small variation around an average of about 8-8.5%. It started decreasing gradually after 60th pulse. However, it should be mentioned that signals for ^{18}O -enriched maleic anhydride ($m/e = 100, 102, 104$) became very weak after 60th pulse, which made it very difficult to integrate these peaks with high accuracy. This also explains the high degree of variability observed after 60th pulse for ^{18}O content. Throughout this experiment no ^{18}O incorporation was observed in furan as well as methyl vinyl ketone. Unlike these products, ^{18}O content of carbon dioxide showed a gradual decrease from its initial value of 4% to 0% by the end of the experiment.

Figure 3 shows the yields of various oxygenated products as a function of n-butane pulse number. Initially, maleic anhydride, furan, methyl vinyl ketone, and carbon dioxide were observed. However, with increasing pulse number production levels for all the products decreased considerably. By 165th pulse, production of maleic anhydride fell below detectable levels. The decrease in the carbon dioxide yield was rapid

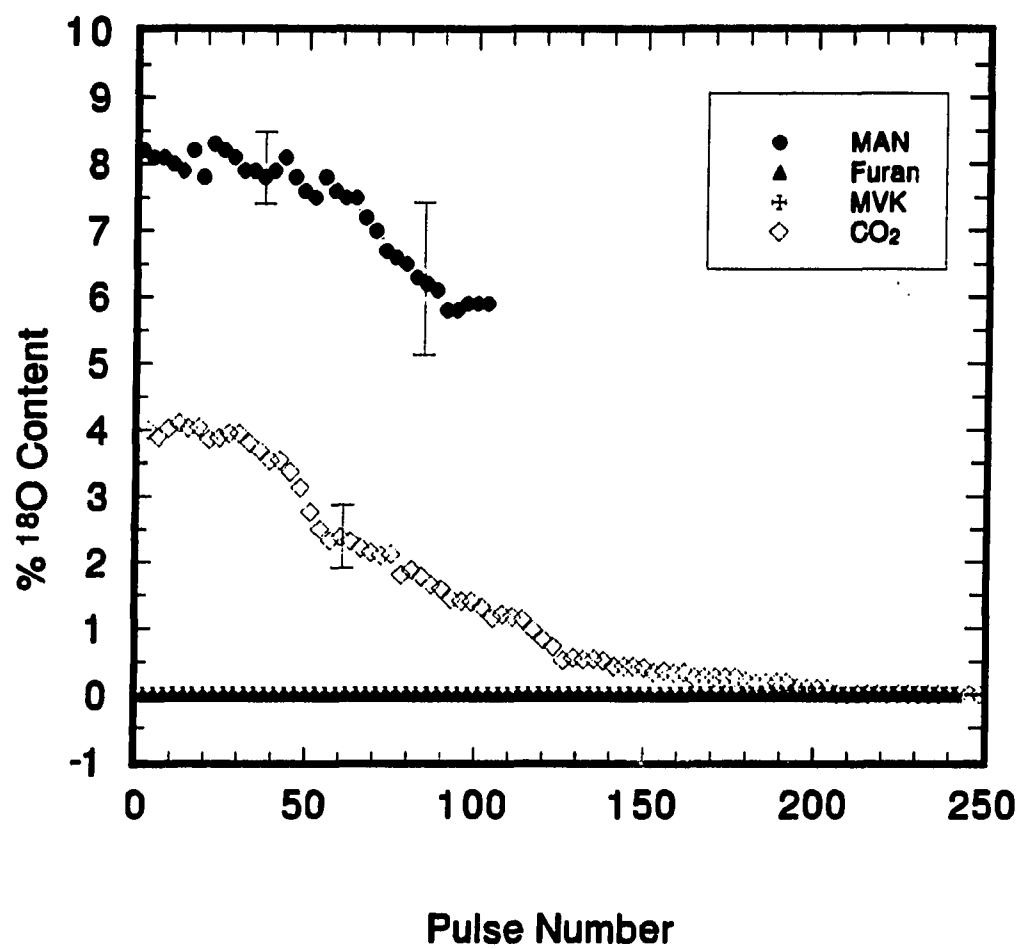


Figure 2: Incorporation of ^{18}O into the oxygenated products of anaerobic oxidation of n-butane by ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst

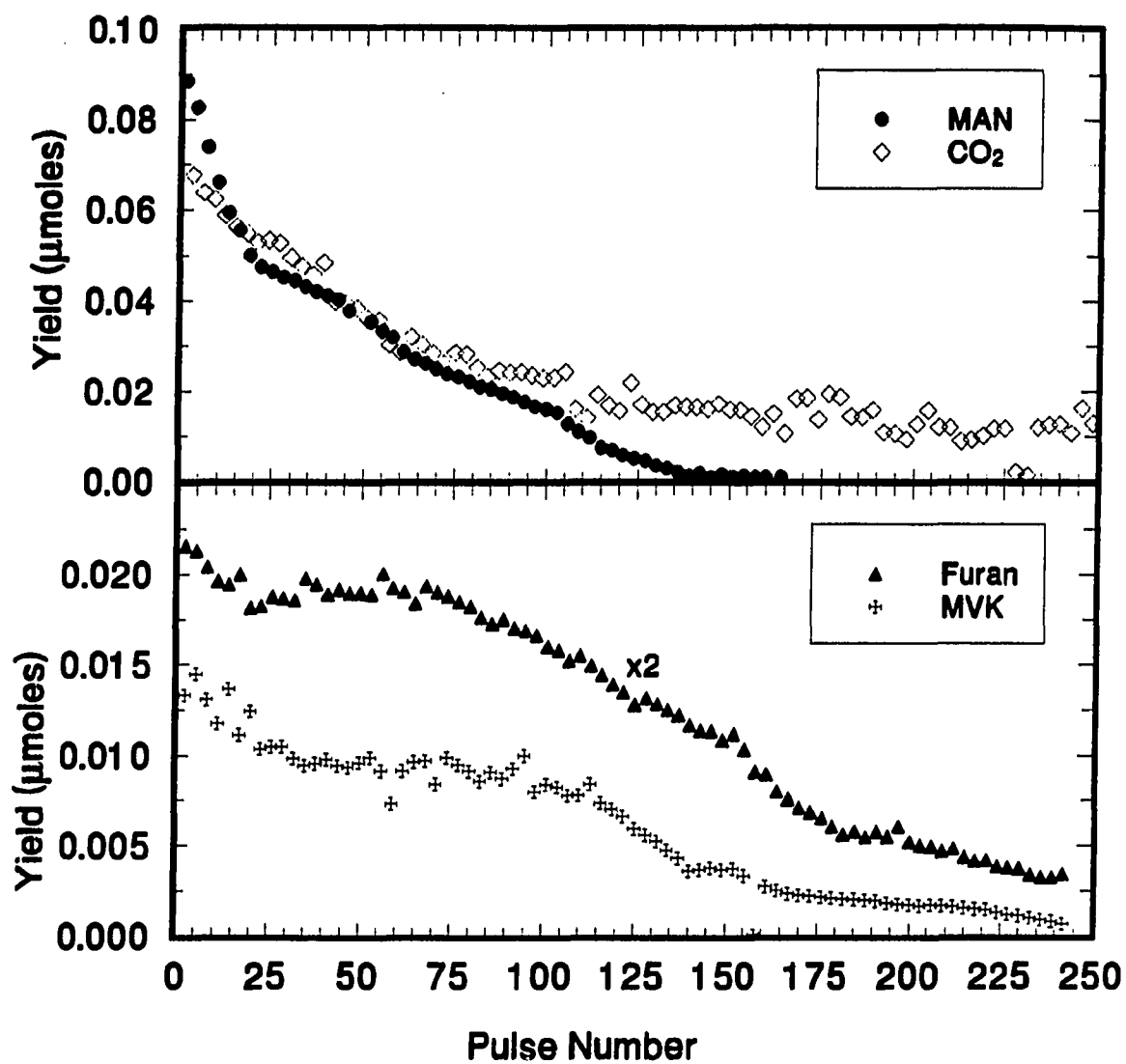


Figure 3: Yields of various oxygenated products of anaerobic oxidation of n-butane by the labeled $(VO)_2P_2O_7$ catalyst

at first, but after about 110 pulses it was much more gradual and showed a lot of variation. Trends in the yields of furan and methyl vinyl ketone were very identical. In both cases, yields decreased initially, then were constant for about 75 pulses before again a gradual decrease. After 240 pulses, yield of methyl vinyl ketone fell below detectable levels. By about 250 pulses, production levels of furan and carbon dioxide were decreased to less than 10% of their initial values. Towards the end of the experiment, 1-butene and 1,3-butadiene were also detected to form, however at negligibly low levels. Total yield of maleic anhydride formed during this experiment was about 4.11 μmole . The yields of furan and methyl vinyl ketone were 1.54 and 1.40 μmole respectively. A total of about 6.08 μmole of carbon dioxide was produced by 250th pulse.

Oxidation of Carbonaceous Deposits

As described earlier, to determine if any carbonaceous deposits are formed during anaerobic consecutive n-butane pulses, two experiments were carried out. In the first experiment, total carbon dioxide formed during the oxygen pulses was determined to be 0.049 μmole . For second experiment this was found to be 0.192 μmole .

Alternate n-Butane/ $^{16}\text{O}_2$ Pulses over the Labeled $(\text{VO})_2\text{P}_2\text{O}_7$

Maleic anhydride, furan, methyl vinyl ketone and CO_2 were all produced from all n-butane pulses, when n-butane and $^{16}\text{O}_2$ pulses were alternated over the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ at 500 C. Considerable amount of CO_2 was produced during oxygen pulse,

following n-butane pulse over the catalyst. However, no other hydrocarbon was observed.

The trends in the yields of oxygenated products were dramatically different, when compared that observed during anaerobic studies for n-butane. These results are presented in Figure 4. Production levels of maleic anhydride during the very first pulse was similar to that observed when only n-butane was consecutively pulsed over the catalyst.

However, during the next few pulses, the production jumped by about 70%, and then it stayed at this level for rest of the experiment. Production levels for both, furan and methyl vinyl ketone were nearly constant through out the experiment. These levels were about 2-3 larger than times those observed during the initial n-butane pulses of the anaerobic studies. Initial high yields of CO₂ decreased gradually to about its half by 20th n-butane pulse, and stayed there for rest of the experiment. For CO₂, total yield i.e., sum of the yields formed during the n-butane and oxygen pulses, was about 8-10 times to that formed during the anaerobic studies. The CO₂ formed during the oxygen pulse was about 5-6 times that of the CO₂ formed during n-butane pulse.

Figure 5 shows the trends in the ¹⁸O content of various oxygenated product formed during the n-butane pulses. The ¹⁸O content of maleic anhydride decreased rapidly from an initial value of about 8% to 1% by the end of the experiment. For CO₂, the initial 4 % ¹⁸O content decreased to 0.5% in the same duration. No ¹⁸O incorporation was observed in furan as well as methyl vinyl ketone through out this experiment.

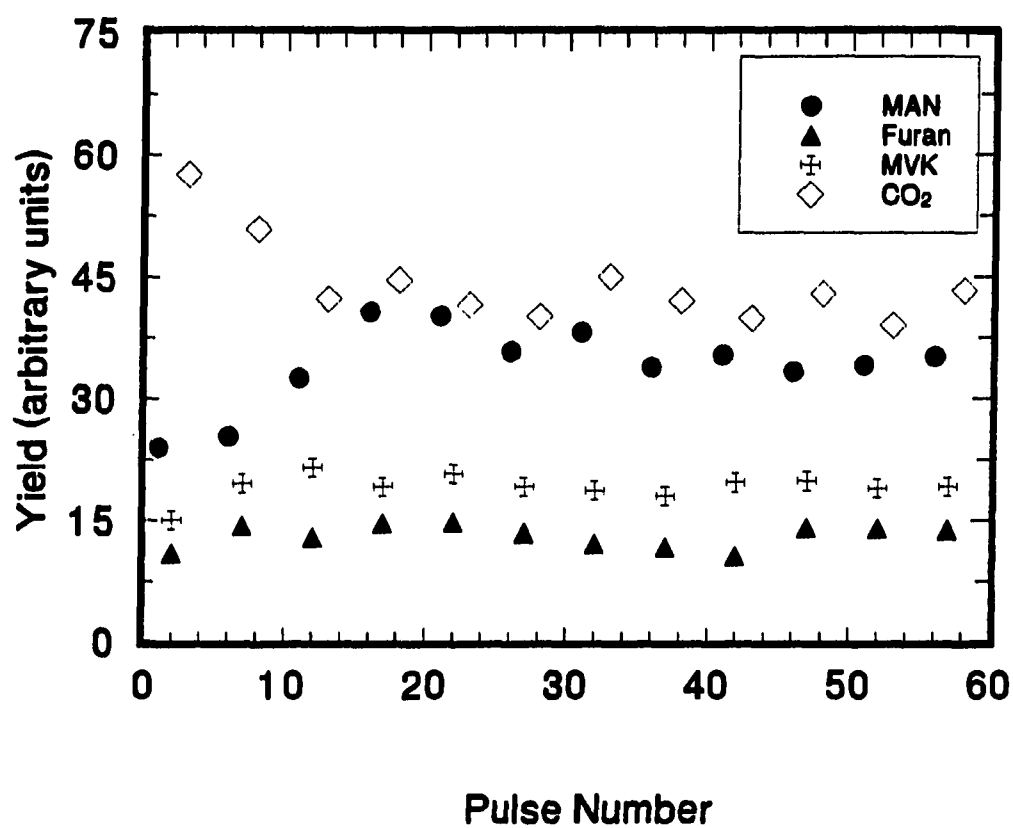


Figure 4: Yields of various oxygenated products formed during the alternate n-butane/¹⁶O₂ pulses over the labeled (VO)₂P₂O₇ catalyst

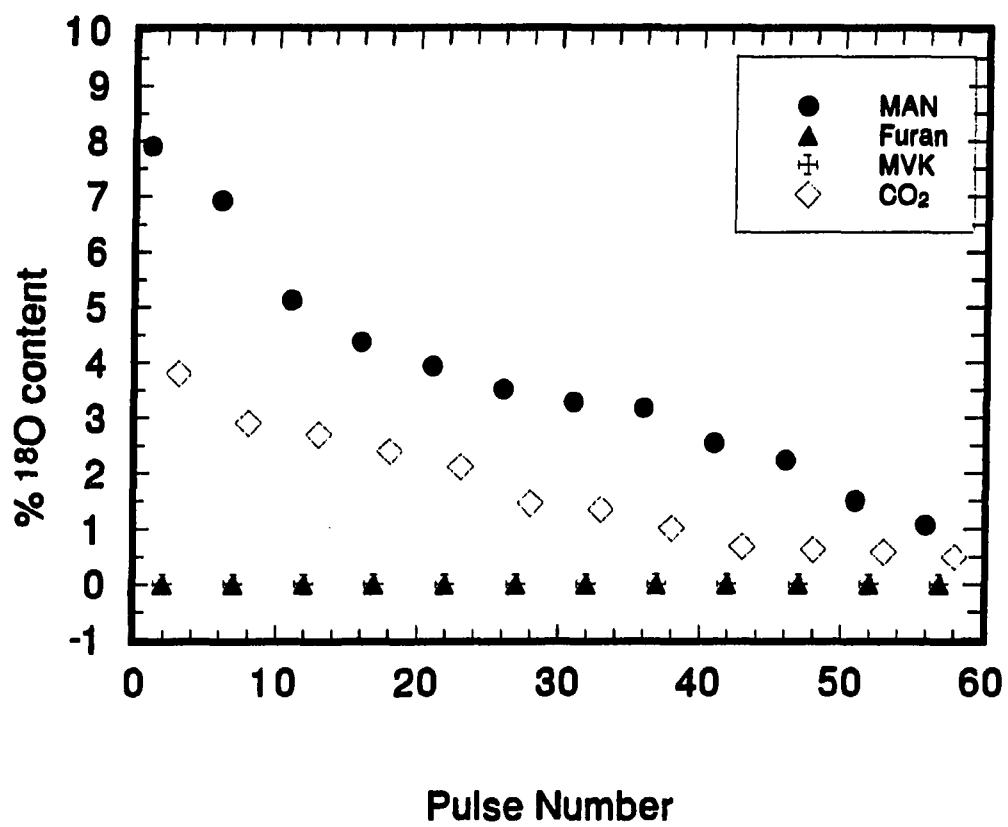


Figure 5: ^{18}O content of various oxygenated products formed during the alternate n-butane/ $^{16}\text{O}_2$ pulses over the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst

Anaerobic Oxidation of 1-Butene by the Labeled $(VO)_2P_2O_7$

The results of anaerobic oxidation of 1-butene pulses by ^{18}O -labeled $(VO)_2P_2O_7$ at 450 C, are shown in Figures 6 and 7. Only furan and carbon dioxide were produced in substantial quantities during this experiment. Maleic anhydride was seen only during very first pulse. Phthalic anhydride was observed for first nine pulses. Yields of both of these products were negligibly low. No methyl vinyl ketone was detected throughout the experiment.

Figure 6 shows the trends in the ^{18}O content of furan and carbon dioxide formed during 1-butene pulses. For furan, a continuous decrease was observed from an initial value of about 17% to about 7% by 365th pulse. The rapid decrease in the furan yield (Figure 6) did not allow an accurate calculation its ^{18}O content after 365th pulse. For carbon dioxide, the decrease in ^{18}O content was much more gradual; starting from 2% initially, by 220th pulse no ^{18}O -labeled carbon dioxide was observed.

As shown in Figure 7, the furan production showed considerable variation around an average value of about 0.016 μ mole for about first 250 pulses before starting a rapid decrease to about 10% of its initial value by 365th pulse, after which the decrease was much more gradual. The production level of carbon dioxide was almost constant for first 300 pulses before a gradual decrease was observed. By 500th pulse, total yield of carbon dioxide was about 9.23 μ mole. For furan this value was determined to be 5.69 μ mole.

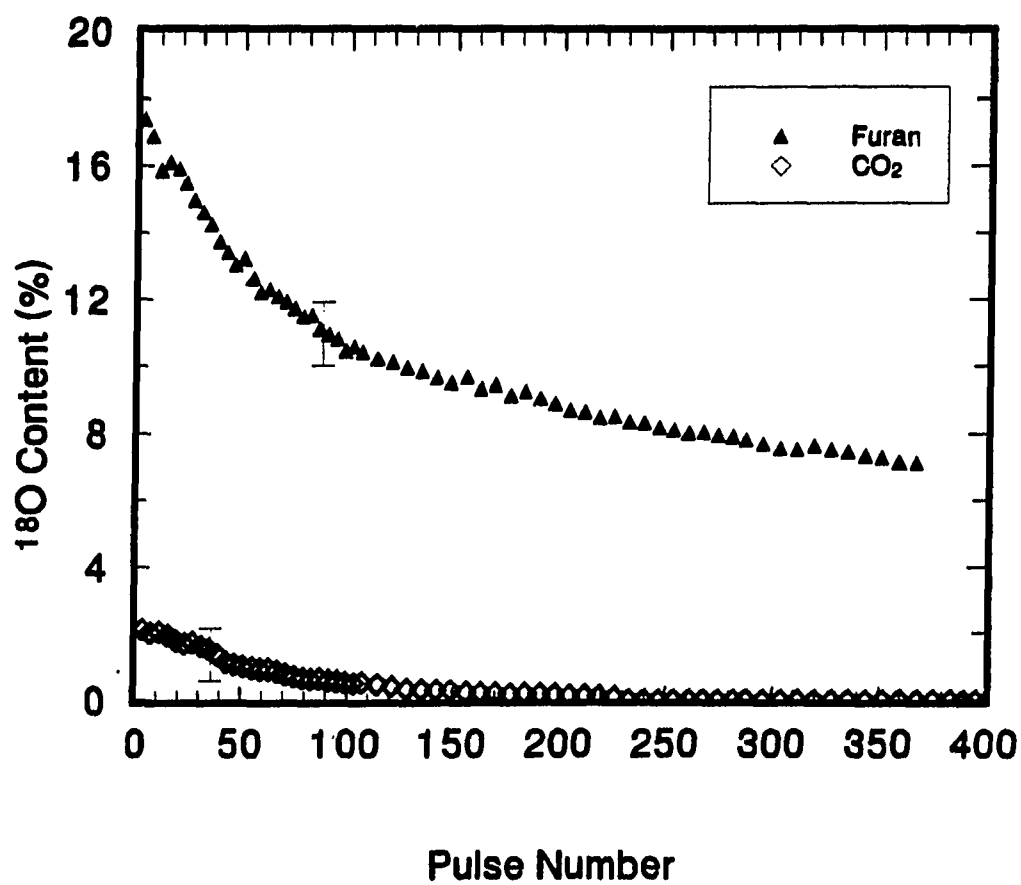


Figure 6: Incorporation of ^{18}O into the oxygenated products of anaerobic oxidation of 1-butene by the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst

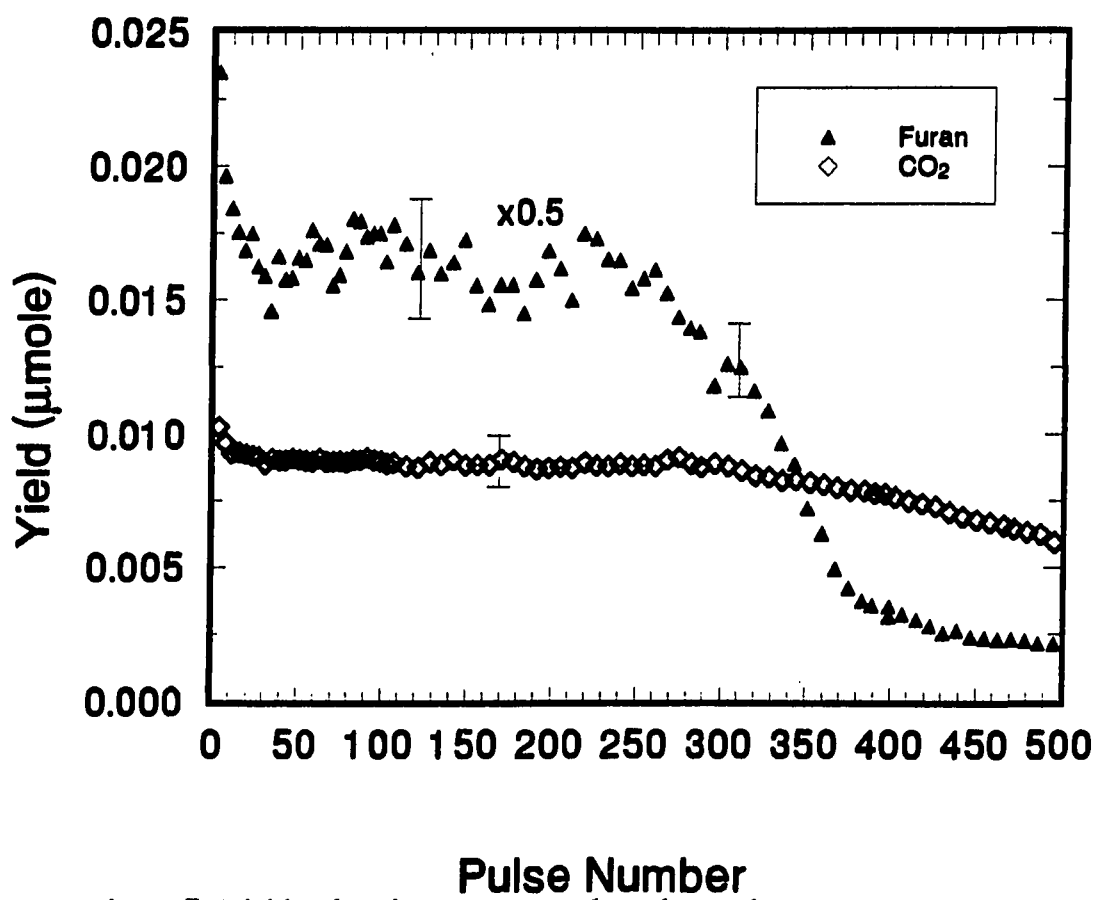


Figure 7: Yields of various oxygenated products of anaerobic oxidation of 1-butene by the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst

Alternate 1-Butene/ $^{16}\text{O}_2$ Pulses over the Labeled $(\text{VO})_2\text{P}_2\text{O}_7$

Unlike the anaerobic 1-butene pulse studies, where only furan and CO_2 were observed, during the alternate 1-butene/ $^{16}\text{O}_2$ pulse study over the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ at 450 C, maleic anhydride was also formed and in substantial quantities. A preliminary study showed that, the amount of maleic anhydride formed depends strongly on the time interval between the oxygen and 1-butene pulses. The trends in the yields of the oxygenated products are presented in Figure 8. The yield of maleic anhydride was constant throughout the experiment. For furan, the yield increased during initial 15 pulses before stabilizing. The yield of furan produced during these pulses was about 10 times that produced during initial 1-butene pulses of the anaerobic studies.

The ^{18}O content of maleic anhydride decreased from about 5% to 1% by the 60th pulse. Very similar trend in ^{18}O content was also observed for carbon dioxide. It decreased from about 5% to 0.5% during this period. The decrease in ^{18}O content was much more gradual for furan. From an initial value of about 13.5%, it dropped to 7% by the end of the experiment. These results are presented in Figure 9.

Chemisorption of Oxygen

The pulsing of oxygen over ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ at 450 C resulted in an oxygen uptake of about 0.92 μmole by the catalyst. At the end of the pulsing, the catalyst temperature was raised to 760 C at a linear rate of about 40 C/min. No appreciable amount of oxygen was detected to leave the catalyst during this period.

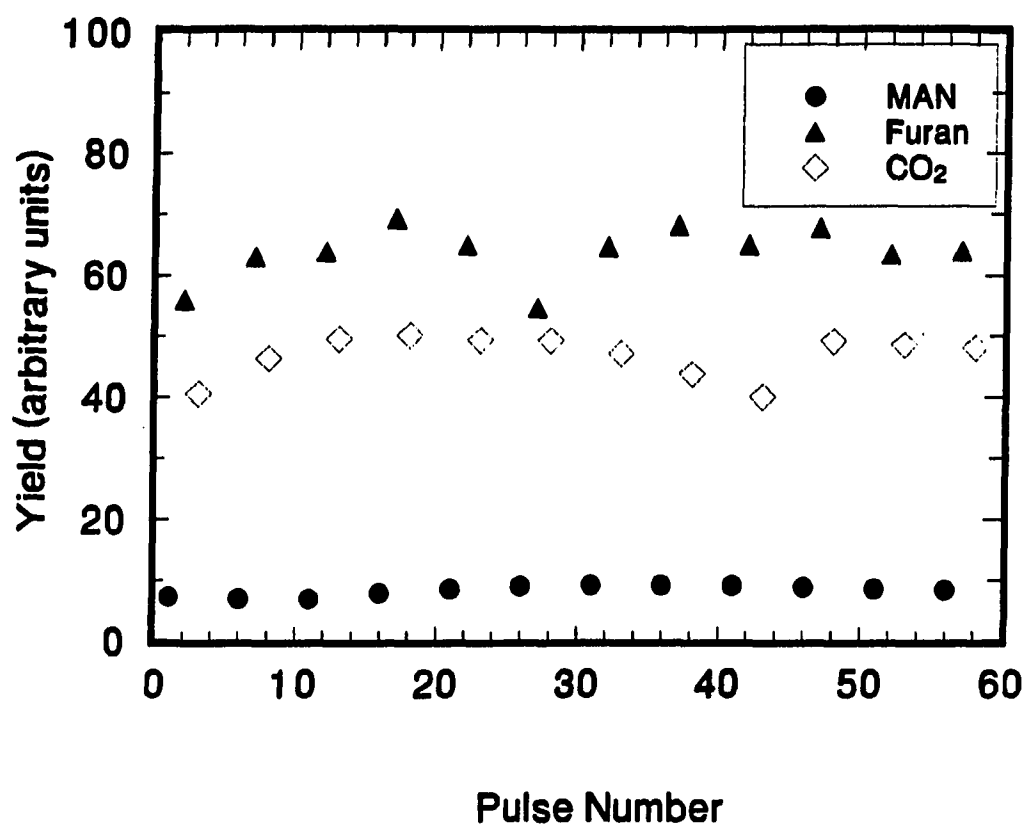


Figure 8: Yields of various oxygenated products formed during the alternate 1-butene/¹⁶O₂ pulses over the labeled (VO)₂P₂O₇ catalyst

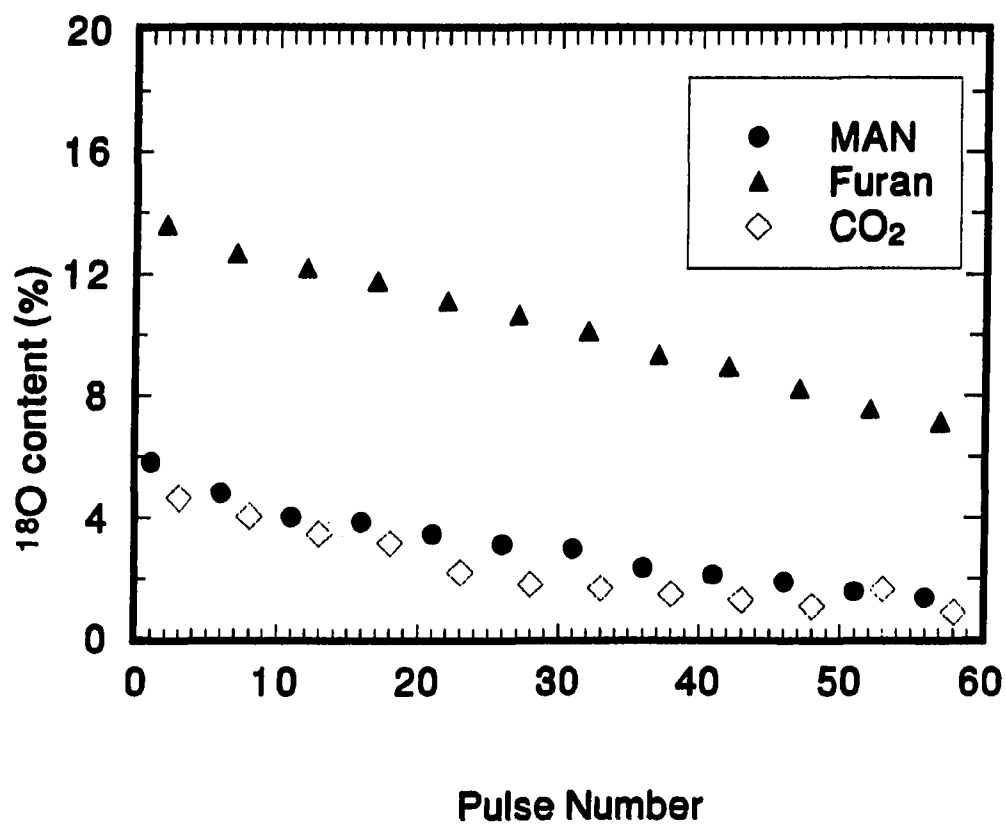


Figure 9: ^{18}O content of various oxygenated products formed during the alternate 1-butene/ $^{16}\text{O}_2$ pulses over ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst

DISCUSSION

Catalyst Structure

Based on the laser Raman and infra red spectroscopical characterization of the labeled catalyst, the location and the extent of ^{18}O incorporation into specific lattice oxygen sites was determined and reported earlier [14]. This ^{18}O distribution in [020] plane in the idealized bulk structure of $(\text{VO})_2\text{P}_2\text{O}_7$ is shown in Figure 10. The average ^{18}O content of P-O-V sites is about 14%. No labeling was found to occur at P-O/ $^{\text{V}}$ -V sites, thus the average of P-O-V sites including the P-O/ $^{\text{V}}$ -V sites is about 9%. The P-O-P sites contains about 30% ^{18}O . The V=O site is not labeled.

Reaction Pathways

The approach employed in this study is similar to that developed in an earlier study with a ^{18}O -labeled $\beta\text{-VOPO}_4$ catalyst [13]. It consists of combining the anaerobic pulse reactor results with the spectroscopic information regarding ^{18}O incorporation into lattice oxygen site, to develop a better understanding of the role of different oxygen sites involved in both the selective as well as nonselective pathways.

The anaerobic oxidation of n-butane by the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ resulted in the preferential incorporation of ^{18}O into maleic anhydride as compared to CO_2 . During the first 50 pulses, the ^{18}O content of maleic anhydride was 8-8.5%, nearly twice than that for CO_2 .

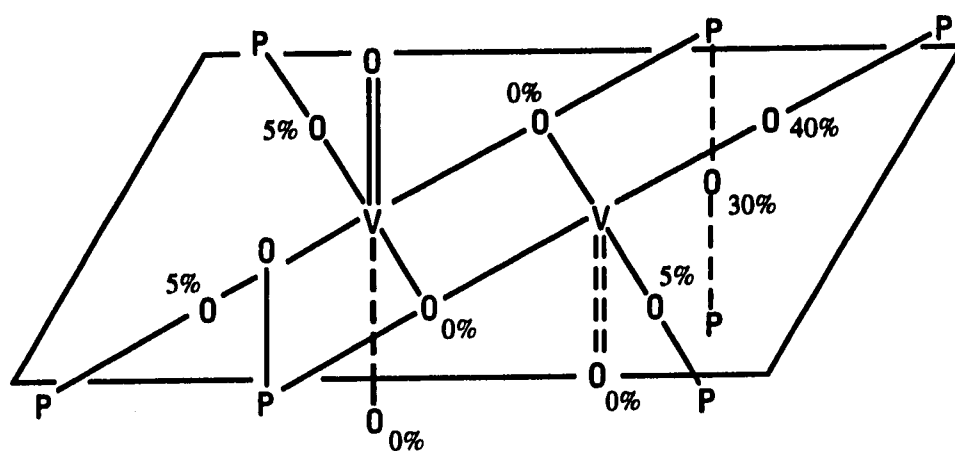


Figure 10: Distribution of ^{18}O in the labeled $(\text{VO})_2\text{P}_2\text{O}_7$ [12]

To account for this selective incorporation, catalyst must contain a "pool" of oxygen sites containing about 8-8.5% ^{18}O . As discussed earlier, based on the spectroscopical characterization of this catalyst, a combination of the P-O-V sites do exist on this catalyst which contain about 9.2% ^{18}O . This pool is made of three P-O-V sites which contain 5% ^{18}O , a P-O-V site labeled to 40%, and two unlabeled P-O/ $^{\text{V}}$ -V sites. This combination could thus provide the required oxygen used in oxygen insertion steps. However, it should be realized this will require these sites to have similar reactivity. It is possible that at high temperatures at which this reaction is carried out, these sites becomes structurally similar and thus enhance the activity equivalence, particularly on the catalyst surface. Throughout the anaerobic *n*-butane pulse oxidation, no ^{18}O incorporation was observed in furan. Both P-O/ $^{\text{V}}$ -V and V=O sites are not labeled with ^{18}O , and thus can provide this oxygen used in ring insertion step. However, furan is a known intermediate for *n*-butane to maleic anhydride conversion. Hence, one can expect that the site that provide oxygen that is used ring oxygen in the furan-like intermediate formed during the maleic anhydride production must be the same site which provide oxygen in intermediate formed during the furan production. Furthermore, the P-O/ $^{\text{V}}$ -V site was earlier proposed to provide oxygen inserted to *n*-butane molecule along with rest of the P-O-V sites. Thus, the P-O/ $^{\text{V}}$ -V site must be providing the oxygen used in ring insertion. An important implication of this ^{18}O incorporation is the specificity of this reaction. The arrangement of various sites required for such *n*-butane conversion to maleic anhydride can be provided by [020] plane alone. This fact therefore explains the high selectivity to maleic anhydride observed for the $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst

with the strongest [020] plane signal in X-ray diffraction pattern [18].

The similarities in the trends of ^{18}O content as well as the yields of both maleic anhydride and CO_2 are very striking. For both maleic anhydride and CO_2 , the ^{18}O content is more or less constant initially, and both start decreasing at about the same pulse number (around 40th pulse). A closer look at the yields of these products shows that they are decreasing initially almost identically. However, by 75 pulses the maleic anhydride yield has decreased about 80-90% of its initial value, while after 75 pulses, the CO_2 yield remained nearly constant for the rest of the experiment. Furthermore, the ^{18}O content of CO_2 was less than 1 % during this time.

These observations strongly suggest that carbon oxides are likely produced by at least two pathways under these pathways. One pathway-the combustion of the maleic anhydride or partially oxidized intermediates may give rise to non-zero ^{18}O content of CO_2 observed during the initial pulses. Another pathway is the direct combustion of n-butane by the surface layer oxygen sites, which are not labeled by ^{18}O . These can be either P-O/V-V or the highly reactive V=O sites. Since all the P-O-V sites were required to be equivalent from earlier discussion, if any of P-O-V site was involved in CO_2 production, the ^{18}O content of CO_2 would have been about 9%. Hence it is only logical to conclude that V=O sites provide the combustion function. These sites have been previously identified by Garbassi and coworkers as being strongly electrophilic sites on the $(\text{VO})_2\text{P}_2\text{O}_7/2$ catalyst [19]. These sites therefore can be possibly involved in an electrophilic attack on n-butane molecule at carbon-carbon bonds thereby leading to highly reactive cracking products which then can undergo further

combustion reactions. The near zero ^{18}O content of carbon dioxide seen after the maleic anhydride production has stopped, clearly indicates that the complete combustion proceeds exclusively on $\text{V}=\text{O}$ sites.

These results combined with the present understanding of this system allow to propose a mechanism for the conversion of n-butane to maleic anhydride as presented in Figure 11. Pepera et al. [13] have proposed that the irreversible activation of a methylene carbon-hydrogen bond in n-butane at a surface $\text{V}(\text{IV})$ site, based on their deuterium-labeled n-butane studies. Activation of n-butane has been suggested by Busca et al. [20] to involve V dimer sites. Bordes [21] have proposed that the n-butane activation may involve a $\text{V}(\text{IV})$ of V dimer site, with breaking of the C-H bond of methylene group, the hydrogen of which is caught by $\text{OH}-(\text{V}=\text{O})$ of the V-V dimer site. This is illustrated in Figure 11.a. The dehydrogenated n-butane-like surface intermediate then reacts with the $\text{P-O}^{\text{V}}\text{-V}$ site to form a furan-like surface intermediate (Figure 11.b). Probably under reduced conditions, some of this species may desorb as gas-phase furan. Further incorporation of oxygen occur at sites involving the (^{18}O -labeled) P-O-V sites to produce maleic anhydride (Figure 11.c). The nonselective pathways may involve some combustion of the maleic anhydride or oxygenated intermediate mostly at the highly reactive $\text{V}=\text{O}$ sites. The total combustion products can also be formed from the cracking of n-butane at $\text{V}=\text{O}$ sites, with the cracking products reacting with all available surface layer oxygen sites, probably including the unlabeled P-O-V sites.

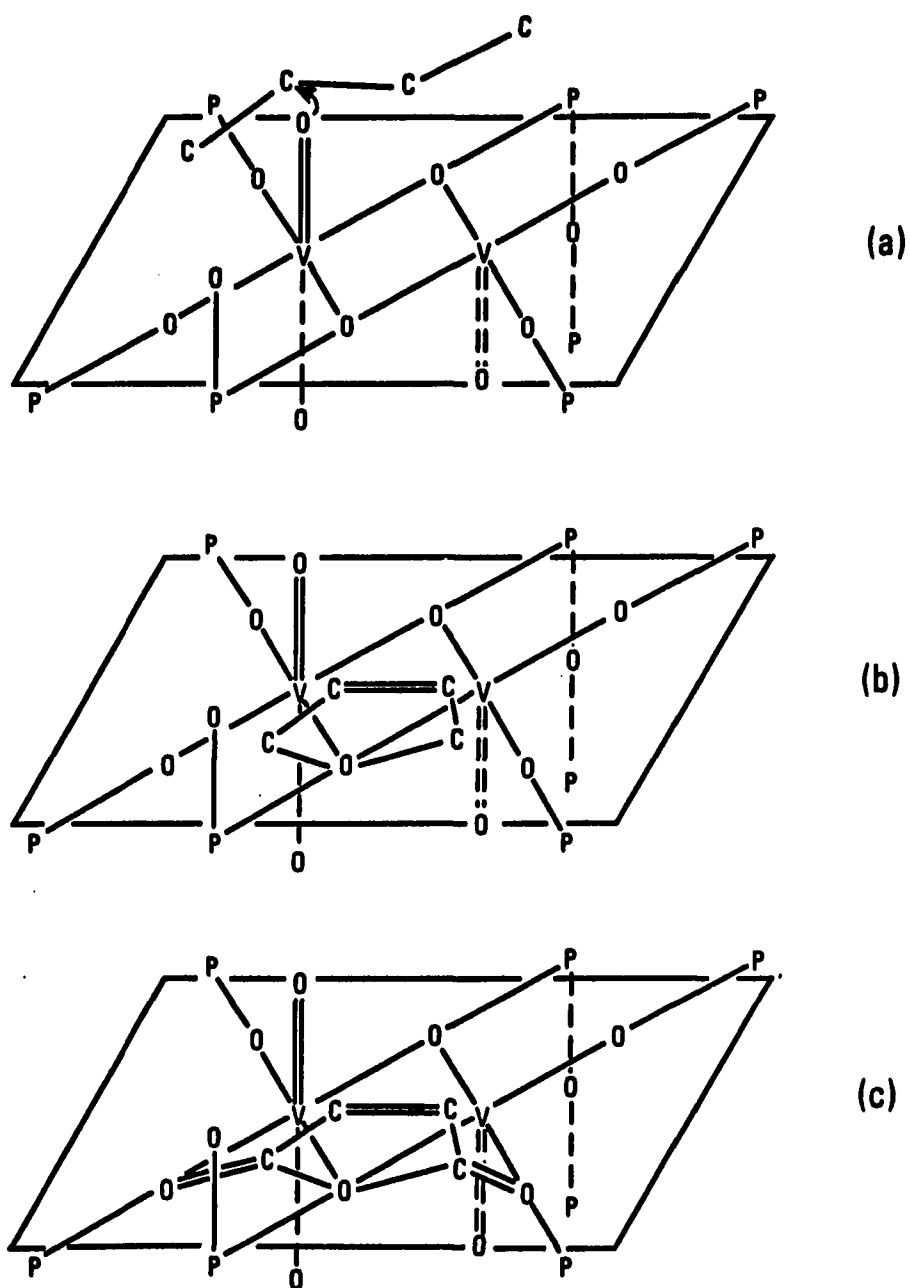


Figure 11: Proposed mechanism for the selective oxidation of n-butane to maleic anhydride over the $(VO)_2P_2O_7$ catalyst

Unlike n-butane, in the case of 1-butene oxidation only furan and carbon dioxide were observed. The gradual decrease in the ^{18}O content of furan indicated the possibility of mobility of the surface oxygen or the fast exchange between different labeled and unlabeled surface layer sites. Nearly 15-16% ^{18}O content seen in furan during the initial anaerobic 1-butene pulse studies, requires a catalyst oxygen source which is labeled to this extent. The combination of P-O-V sites, excluding the P-O/ $^{\text{V}}$ -V sites can act as such source. No such particular assignment of a site could be done for nonselective pathways.

The wide differences in ^{18}O incorporation and the yield patterns of an oxygenated product (viz. furan and CO_2) observed during the n-butane anaerobic oxidation as compared to that of 1-butene anaerobic oxidation studies, clearly indicate that initial interaction of n-butane is fundamentally different than that of 1-butene. This would therefore suggest that "free" 1-butene is not a likely intermediate in the n-butane oxidation.

Participation of Bulk Oxygen

To study the participation of bulk oxygen in the mechanism the catalyst was pulsed with n-butane (1-butene) till no further hydrocarbon conversion was achieved. The total yields of various oxygenated products formed during these studies for n-butane are presented in Table 2 (Table 3 for 1-butene). It also shows these yields expressed as number of monolayers of oxygen used for the production of a particular product formed during this reaction, on the basis of average surface density of V dimer sites (taken as $5.5 \mu\text{mole}/\text{m}^2$). It is clear from this analysis that about 4 monolayers near surface participate in n-butane

Table 2: Yield of the oxygenated products of anaerobic oxidation of n-butane by the labeled $(VO)_2P_2O_7$ catalyst

Product	Total Yields (μmole)	Monolayers ¹
MAN	4.11	1.74
Furan	1.56	0.65
MVK	1.47	0.60
CO ₂	6.08	2.58

1: Based on the average surface density of V dimer sites taken as $5.5 \mu\text{mole}/\text{m}^2$ in the [020] plane of the idealized bulk structure of $(VO)_2P_2O_7$ catalyst.

Table 3: Yield of the oxygenated products of anaerobic oxidation of 1-butene by the labeled $(VO)_2P_2O_7$ catalyst

Product	Total Yields (μmole)	Monolayers ¹
MAN	0.06	0.00
Furan	5.74	3.61
CO ₂	8.48	5.23

1: Based on the average surface density of V dimer sites taken as $5.5 \mu\text{mole}/\text{m}^2$ in the [020] plane of the idealized bulk structure of $(VO)_2P_2O_7$ catalyst.

activation. However, the gradual decrease in the yields of various oxygenated products can be due to either unavailability of oxygen or possible blocking of catalyst active sites due to carbonaceous deposits formed during earlier hydrocarbon pulse. Near constant or sometime even increasing yields of various oxygenated products seen during the alternate hydrocarbon/oxygen pulses would normally indicate that the gradual decrease in yield of these products observed during the anaerobic studies was due to lack of readily available oxygen from the catalyst. However, very large amounts of carbon dioxide as well as increased yields of maleic anhydride and furan during the alternate n-butane/oxygen studies also indicate (1) possible presence of partially oxidized hydrocarbon species, and (2) formation of a highly reactive oxygen species on the catalyst surface during the oxygen pulses. The results of the dynamic oxygen chemisorption experiments clearly indicate that it is an irreversibly chemisorbed oxygen, and was also observed to form by other workers in this area [11, 12]. The experiments carried out to determine the extent of carbonaceous deposits formed after a single n-butane pulse showed that about 2% of surface V-V dimer sites would be covered by carbon dioxide formed during the oxygen pulses. However, after 100 consecutive n-butane pulses, only 9% of these sites were found to be covered by the carbon dioxide. This clearly indicates that the carbonaceous deposits accumulated during the n-butane pulses did not cause the sharp decrease in the production of oxygenated products during anaerobic n-butane oxidation. This therefore would imply that the bulk oxygen of $(VO)_2P_2O_7$ does not readily replenish the reduced surface layer oxygen sites on the time-scale of this experiment.

The dynamic chemisorption experiments were done under otherwise identical conditions as anaerobic C₄ hydrocarbon oxidation, except that instead of the n-butane pulses, oxygen pulses were introduced on the catalyst. Thus, the oxygen interacted with the identical catalyst surface that otherwise n-butane would have interacted. Hence, the observed irreversible chemisorption indicate that catalyst surface was not oxidized when n-butane was pulsed on the catalyst under anaerobic conditions, and the observed oxidation activity is due to the catalyst oxygen itself.

Finally, it should be realized that these studies emphasize the reactivity of the surface layer sites of a fresh catalyst under anaerobic conditions. As evident from the alternate C₄ hydrocarbon/O₂ studies, adsorbed oxygen seems to play important role not only in catalyst reoxidation but also in activation and subsequent oxidation steps. Therefore, in the presence of gas-phase oxygen, such as in an industrial reactor, a more complex mechanism involving several types of oxygen species could be expected.

CONCLUSIONS

The role of various reactive sites in the oxidation of C_4 hydrocarbons with β -(VO)₂P₂O₇ was investigated using isotopic reactive-site mapping (IR-SM) technique. It allowed to associate specific surface oxygen sites with the reaction pathways for selective and nonselective oxidation. New information regarding the mechanistic details was obtained.

According to these studies, n-butane is chemisorbed and activated at the V dimer sites of (VO)₂P₂O₇ catalyst in an irreversible and very specific manner. As evident from other work, this may result in a highly constrained, partially dehydrogenated olefin-like species. This species then can undergo oxygen insertion at a nearby V-O^P-V site to form a furan-like surface intermediate, which under oxygen deficient conditions may desorb as furan. Additional reaction and oxygen insertion at P-O-V sites leads to the production of maleic anhydride. Combustion products seems to be formed by several pathways: either by combustion of the intermediates or maleic anhydride or the direct oxidation of n-butane, first involving its cracking at V=O sites.

Participation of bulk oxygen was studied by conducting quantitative IR-SM studies. These studies indicated that bulk oxygen is not capable of quickly replenishing the surface reduced sites, and that the redox mechanism is limited to surface monolayer. It is also evident from these studies that the selectivity of a reactive site depends upon the hydrocarbon feed.

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PAPER III.
NONSELECTIVE PATHWAYS IN THE OXIDATION OF C₄ HYDROCARBONS
OVER β -(VO)₂P₂O₇ CATALYST

ABSTRACT

A ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst was used to investigate the nonselective pathways in the catalytic oxidation of C_4 hydrocarbons over the $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst. Alternate hydrocarbon/oxygen pulse studies allowed to determine the nature of the surface hydrocarbon intermediate formed during the anaerobic oxidation. These studies were then modified to study the complete oxidation of this intermediate to carbon oxides. These results point to an irreversibly chemisorbed species which is significantly oxidized. Both short-lived adsorbed dioxygen and irreversibly chemisorbed oxygen were found to be capable of completely oxidizing this intermediate. Furthermore, the oxidation of this intermediate by gas-phase oxygen seems to be a step-wise process. Similar results were observed for 1-butene, but as expected, the surface intermediate is more oxidized than in the case of n-butane.

INTRODUCTION

Selective oxidation of n-butane over the vanadium-phosphorus-oxide (V-P-O) catalysts have been widely investigated, because of its industrial importance as a major processing route for the production of maleic anhydride [1-3]. This is one of the few commercially successful examples of chemical utilization of alkanes. Thus, it also serves as a useful model for determining other possible selective oxidation reactions of alkanes, which are abundantly available as cheap raw materials.

Initial investigations in this area have correlated the catalytic performance of these catalysts with the synthesis and activation techniques [3-5]. These studies have demonstrated the importance of P-to-V ratio, oxidation state and structural characteristics on the catalyst performance. It is generally accepted that vanadyl pyrophosphate, $(VO)_2P_2O_7$, is the most active and selective of V-P-O phases, and is present in the industrial catalysts [6-8]. More recently, studies in this area have focussed on the defining the selective pathways, detection of the possible intermediates, and the nature of the active sites in the redox mechanism [9-11]. In general, these studies have made significant contributions to the understanding of the redox mechanism of the C_4 oxidation over $(VO)_2P_2O_7$ catalyst.

Nonselective pathways which lead to carbon oxides have been the subject of numerous studies in this area. Based on kinetic studies, two pathways have been proposed for the formation of carbon oxides: (1) the direct oxidation of n-butane to CO and CO_2 , and (2) the

consecutive oxidation of maleic anhydride to CO and CO₂ [12, 13]. Results of the recent mechanistic studies suggest similarly. Centi et al. [14] have demonstrated that parallel to the selective activation mode, nonselective routes involving different sites are present. One such route was proposed to involve an adsorbed dioxygen species. Their studies involved blocking of oxygen sites by ammonia during n-butane oxidation over (VO)₂P₂O₇ catalyst. Moser and Schrader [15] on the other hand, have investigated the oxidation of maleic anhydride feed with the fresh (VO)₂P₂O₇ catalyst using an integral reactor. These studies provided clear evidence for the complete combustion of maleic anhydride under typical industrial process conditions. It thus proved the existence of the second pathway to CO₂.

An area still not well understood is the nature of the oxygen species involved in these pathways. Kruchinin et al. [16] have monitored the ¹⁸O incorporation from the gas phase into CO and CO₂ in a closed recirculating system over a VPO catalyst containing cobalt. They observed a gradual incorporation of ¹⁸O in these products, indicated that oxygen from the lattice was being directly used to produce CO and CO₂. Similar studies were carried out by Pepera et al. [17] with (VO)₂P₂O₇ catalyst. Their experiments involved equilibrating the catalyst surface with ¹⁸O, and then monitoring its incorporation in CO₂ formed during the subsequent n-butane pulses. These investigators suggested that redox (reduction-oxidation) mechanism involves only near surface layers. Ebner and Gleaves [18] have used TAP (temporal analysis of products) reactor system to study the nature of the nonselective oxygen. Their time-resolved double pulse experiments involved pulsing a mixture of ¹⁸O-cis-2-butene over an equilibrated (VO)₂P₂O₇ catalyst and monitoring the CO₂ temporal curves of the

various isotopes. These studies led them to suggest two sources of oxygen for the formation of CO_2 : a "fast" source identified as a highly reactive short-lived chemisorbed oxygen is involved in the direct reaction with butene to form CO_2 . Another "slow" source was attributed to surface layer oxygen, the exact nature of which is yet not determined. The surface layer oxygen plays a significant role in producing CO_2 by a much slower process. Chemisorbed oxygen have been implicated in combustion pathways also by Centi et al. [14]. Contractor and coworkers [19] have observed that in the absence of the gas phase oxygen, it is possible to eliminate a highly nonselective oxygen species. This knowledge was core of the new transport bed technology developed by Du Pont for the industrial production of maleic anhydride [20]. This technology separates the oxidation and reduction functions of the catalyst, thereby resulting in high selectivities for maleic anhydride.

In a previous investigation, we have synthesized a $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst with ^{18}O labeled in highly specific oxygen sites [21]. The location and the extent of the ^{18}O was determined from spectroscopic characterization of the catalyst. Catalyst was pulsed with C_4 hydrocarbons under anaerobic conditions while ^{18}O uptake into specific products was monitored. This information allowed to determine the specific surface layer oxygen sites involved in the redox mechanism. In this work, we have slightly modified this technique to study the nonselective pathways and in particular, the nature of the surface hydrocarbon intermediate involved. This work has provided new information regarding the combustion pathways and reoxidation of the reduced catalyst surface.

EXPERIMENTAL PROCEDURE

Catalyst

A ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ was used for investigating the non-selective pathways in the oxidation of C_4 hydrocarbons. It was synthesized using a three steps procedure described earlier [21]. Infra red and laser Raman spectroscopical characterization of this catalyst has shown the ^{18}O labeling to be highly site specific, and its extent has been already been determined.

Pulse Reactor Studies

Reactor studies were carried out with a 1/4 in stainless steel pulse microreactor using 0.2 g of 10-20 mesh pellets of fresh ^{18}O -labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst. The reactor was passivated by first treating it with *o*-phosphoric acid (85%) and then calcining it in flowing oxygen at 550 C for 8 h. The catalyst bed was supported by quartz wool pretreated in a similar fashion. V-P-O catalyst phases are notoriously susceptible to the water vapors and carbon dioxide from the atmosphere [22]. Therefore, after loading the catalyst, it was thermally pretreated using a procedure developed earlier [21]. After the thermal pretreatment, catalyst was cooled to down to reaction temperature (500 C for n-butane and 450 C for 1-butene feeds), and this temperature was maintained for 1 h. Reactant pulses were then introduced in the desired fashion using a 10-port Valco valve, equipped with a 0.5-ml

injection loop for hydrocarbon and 0.5-ml for oxygen. The valve assembly was maintained at 125 C. Pulse compositions and gas flow rates were regulated using Tylan mass flow controllers (Model FC260). Helium (Air Products, zero grade) was used to dilute n-butane and 1-butene (Matheson, instrument grade) to achieve a 6% molar hydrocarbon content. Residual oxygen was removed from these gases using Oxy-trap (Alltech). Oxygen (Air Products, 99.8%) was diluted with helium to give a 21 % molar concentration. Residual water was removed from all these gases using molecular sieve/drierite gas purifiers (Alltech). For isotopic studies involving ^{18}O , ^{18}O (ICON, 99% ^{18}O) samples were injected via a syringe over the catalyst bed through an injection port placed just above the reactor inlet, in the increments of 0.05 cc.

Dynamic adsorption technique was used to study the oxygen chemisorption over labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst at 500 C. Initially, reactor was loaded with 0.2 g of the labeled catalyst, and then thermally pretreated to achieve a clean surface [21]. It was then cooled down to 500 C, and maintained at this temperature for 1 h. Oxygen (10% in He) pulses were then introduced at a rate of 1 pulse per minute. Pulsing was continued till no additional oxygen uptake was observed. The process was monitored by mass spectrometry. Exchange between the gas-phase $^{18}\text{O}_2$ and the catalyst oxygen was also studied in a similar fashion.

The reactor effluent were monitored using a on-line mass spectrometer. A UTI 100C precision quadruple mass analyzer controlled by a HP Vectra personal computer using Spectrasoft (UTI) software. A glass single stage molecular jet separator (SGE, MJSS/ST) was used to interface the mass analyzer with the microreactor system. Molecular jet separator

stripped helium from the reactor effluent, thereby increasing the concentrations of oxidation product. During these experiments, n-butane and 1-butene were monitored using m/e 42. For monitoring oxygen, m/e 32, 34, and 36 were used. Carbon dioxide was monitored using m/e 44, 46 and 48. Interferences at m/e 44 due to background air and n-butane (or 1-butene) fragmentation, and at m/e 48 due to 1-butene were corrected in a straight forward manner based on reference m/e 42.

RESULTS AND DISCUSSION

Oxygen Chemisorption and Exchange

Pulsing of ^{18}O over a thermally pretreated labeled $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst resulted in an $^{18}\text{O}_2$ uptake of about $0.95\ \mu\text{mole}$ by the catalyst at $500\ \text{C}$. When no additional oxygen uptake was observed, catalyst was linearly heated to $760\ \text{C}$ at a linear rate of $40\ \text{C/min}$, and held there for $5\ \text{min.}$ About $0.05\ \mu\text{mole}$ of oxygen desorbed during this procedure. This indicates an irreversible chemisorption of the oxygen corresponding to about 1 oxygen atom per vanadyl dimer site. During these oxygen pulses, no appreciable amount of $^{16}\text{O}^{18}\text{O}$ ($m/e\ 34$) or $^{16}\text{O}_2$ ($m/e\ 32$) was observed, indicating lack of any exchange between the gas-phase $^{18}\text{O}_2$ and catalyst $^{16}\text{O}_2$. This study was also repeated with $^{16}\text{O}_2$ to study the oxygen exchange with catalyst labeled sites. Once again no exchange was observed. Similar results have been reported by other investigators with equilibrated $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst [17, 18]. The lack of oxygen exchange during the oxygen pulse clearly indicates the irreversibility of the chemisorption.

Alternate n-Butane/ O_2 Pulses

Alternate C_4 Hydrocarbon/ ^{16}O pulse studies allow to investigate the nonselective pathways by separating the oxidation and reduction functions of the catalyst. For these studies, $0.2\ \text{g}$ of thermally pretreated fresh catalyst was first pulsed with n-butane (6% in

He), 35 seconds later a oxygen pulse (21 % in He, O_2/C_4 molar ratio = 3.5) was fed to the catalyst bed. Preliminary studies showed that maleic anhydride, furan, methyl vinyl ketone and carbon oxides were formed during the n-butane pulses, whereas only carbon oxides (CO , CO_2) were formed during the oxygen pulses. None of n-butane, 1-butene or 1,3-butadiene were detected during oxygen pulse. Figure 1 shows the results of monitoring m/e 44 (after correcting for n-butane fragmentation and background air), 46 and 48 during the alternate n-butane/ ^{16}O pulses at 500 C. The carbon dioxide formed during the n-butane pulse contained about 3-4% ^{18}O . In a previous report, anaerobic oxidation of n-butane pulses was studied over ^{18}O -labeled $(VO)_2P_2O_7$ catalyst under conditions identical to those used in this study. In that study, we concluded that there are at least two pathways for CO_2 formation. One was shown to be the consecutive combustion of maleic anhydride, while the other was direct combustion of n-butane at highly reactive $V=O$ sites [23]. The carbon dioxide yield observed during the oxygen pulse was about 10-12 times larger than that during the n-butane pulse. Similar studies with different O_2/n -butane ratio showed that the size of the CO_2 peak depends upon a number of parameters, but most strongly on the amount of oxygen pulsed after n-butane pulse. CO_2 production during the oxygen pulse provides clear evidence a strongly chemisorbed (possibly irreversibly) hydrocarbon species is involved in this nonselective pathway. Formation of such carbonaceous materials during the interaction of alkanes with metal oxide surfaces under reduced (oxygen deficient) conditions is a known phenomena [17]. Therefore, it is particularly interesting that even with a fresh catalyst this is observed. An even more interesting feature of these results is that during the oxygen pulse, some $C^{16}O^{18}O$

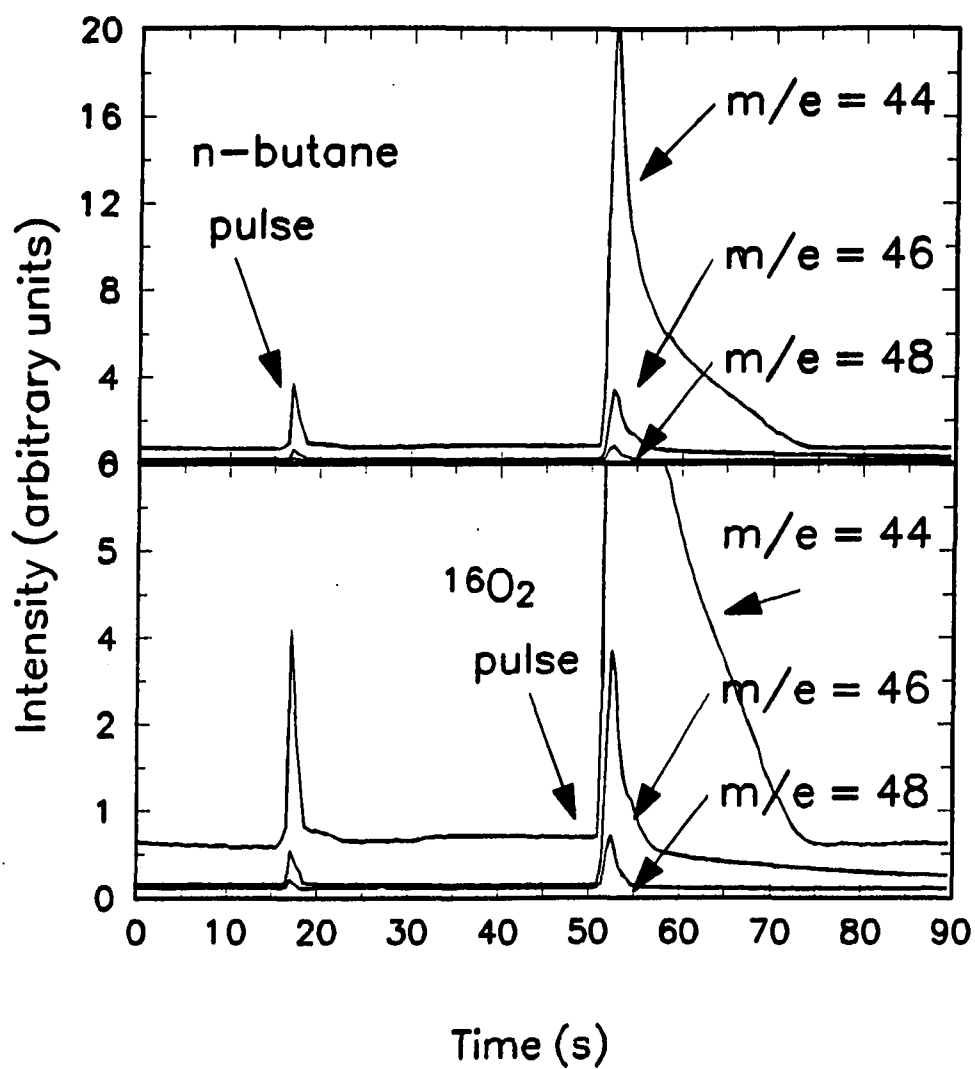


Figure 1: Carbon dioxide production during the alternate n-butane/ $^{16}\text{O}_2$ pulses

and negligibly small amounts $C^{18}O_2$ were formed. Such ^{18}O incorporation into CO_2 can be explained either if the surface hydrocarbon species already contains some ^{18}O in it before it was oxidized to CO_2 by oxygen pulse, or if the reoxidation of catalyst occurs during the oxygen pulses which redistribute the oxygen between the various sites. Such process however, would require a fast exchange between the surface and gas-phase oxygen.

It then became important to determine to what extent is this species oxygenated. It was observed that the amount of the ^{18}O incorporated in CO_2 was dependent upon the amount of oxygen pulsed. Thus, a direct calculation of extent of ^{18}O in CO_2 is not a highly reliable way of finding out the oxygen content of the surface species. Therefore, the original alternate n-butane/ O_2 pulse experiment was slightly modified by injecting ^{18}O instead of ^{16}O . These results are presented in Figure 2. This time a large $C^{16}O^{18}O$ peak (m/e 46) was observed along with a small $C^{18}O_2$ peak (m/e 48), and a sharp $C^{16}O_2$ peak (m/e 44). Each curve has a unique shape, and the maxima of each peak occurred at different times. The $C^{18}O_2$ yield reached its maxima first, thereby indicating it was the fastest process. Furthermore, its peak width was smallest with no tailing which was observed for other two CO_2 (m/e 44 and 46). This evidence points to short-lived adsorbed dioxygen. The ^{18}O content of all the CO_2 produced was determined to be near 22%. This clearly indicates that the surface intermediate species is highly oxidized and contains significant amount of oxygen. Equally interestingly, it also indicates that before the oxidation of the surface species, reoxidation of the catalyst surface seems to occur.

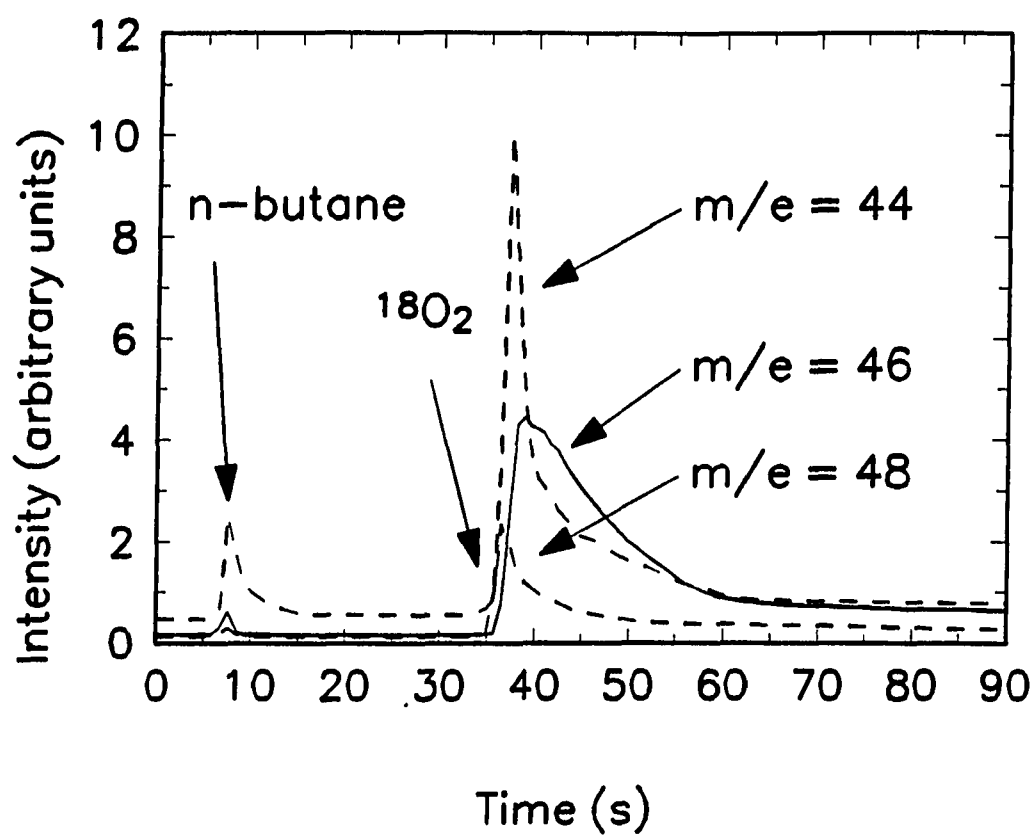


Figure 2: Carbon dioxide production during the alternate n-butane/ $^{18}\text{O}_2$ pulses

Reoxidation of the Catalyst Surface

Reoxidation of the catalyst surface was studied by considerably modifying the above alternate pulse technique. A 0.2 g sample of fresh catalyst was initially thermally pretreated and prepared for the reaction studies as described earlier. 10 consecutive n-butane pulses were then passed through the catalyst bed. About 35 seconds after the tenth n-butane pulse, small oxygen pulses (12%) were introduced till no additional carbon dioxide formation was observed. As seen from Figure 3, during the first oxygen pulse only small amount of CO_2 was formed, however, its production level increased during next few pulses. It maximized during the 3rd pulse, before rapidly decreasing. This is thus, clearly evident of a sequential or a stepwise process for the combustion of the surface hydrocarbon species. It consists of a initial step of oxidation of the reduced catalyst surface which is then followed by the complete oxidation of the surface hydrocarbon species by a chemisorbed oxygen species.

The reoxidation of the catalyst surface was further investigated by once again slightly modifying the above experiment. In this case, ^{18}O was used instead of ^{16}O . Results of this experiment are presented in Figure 4. Though general features were similar to those observed with ^{16}O , quite a few additional interesting features were also observed. First of all, no C^{16}O_2 (m/e 44) was observed during first pulse, while only small isotopically labeled CO_2 (m/e 46 and 48) were produced. With additional ^{18}O pulses, C^{16}O_2 (m/e 44) started to be produced only to maximize during 5th pulse and to decrease thereafter. $\text{C}^{16}\text{O}^{18}\text{O}$ (m/e 46) and C^{18}O_2 (m/e 48) also showed maxima in their production, only at different pulse numbers. These observations clearly confirm a sequential process for combustion of surface species.

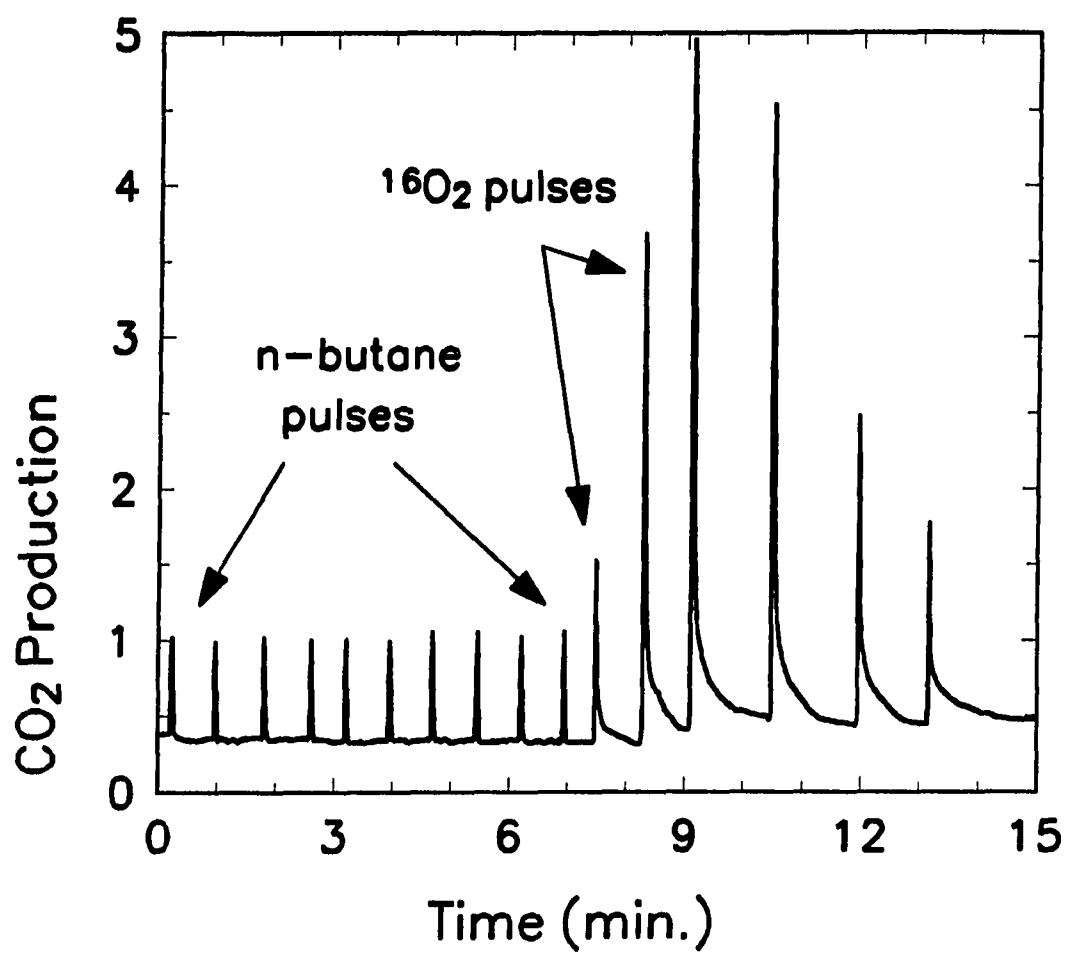


Figure 3: Carbon dioxide production during the reoxidation of the catalyst by ¹⁶O₂ pulses following ten consecutive n-butane pulses

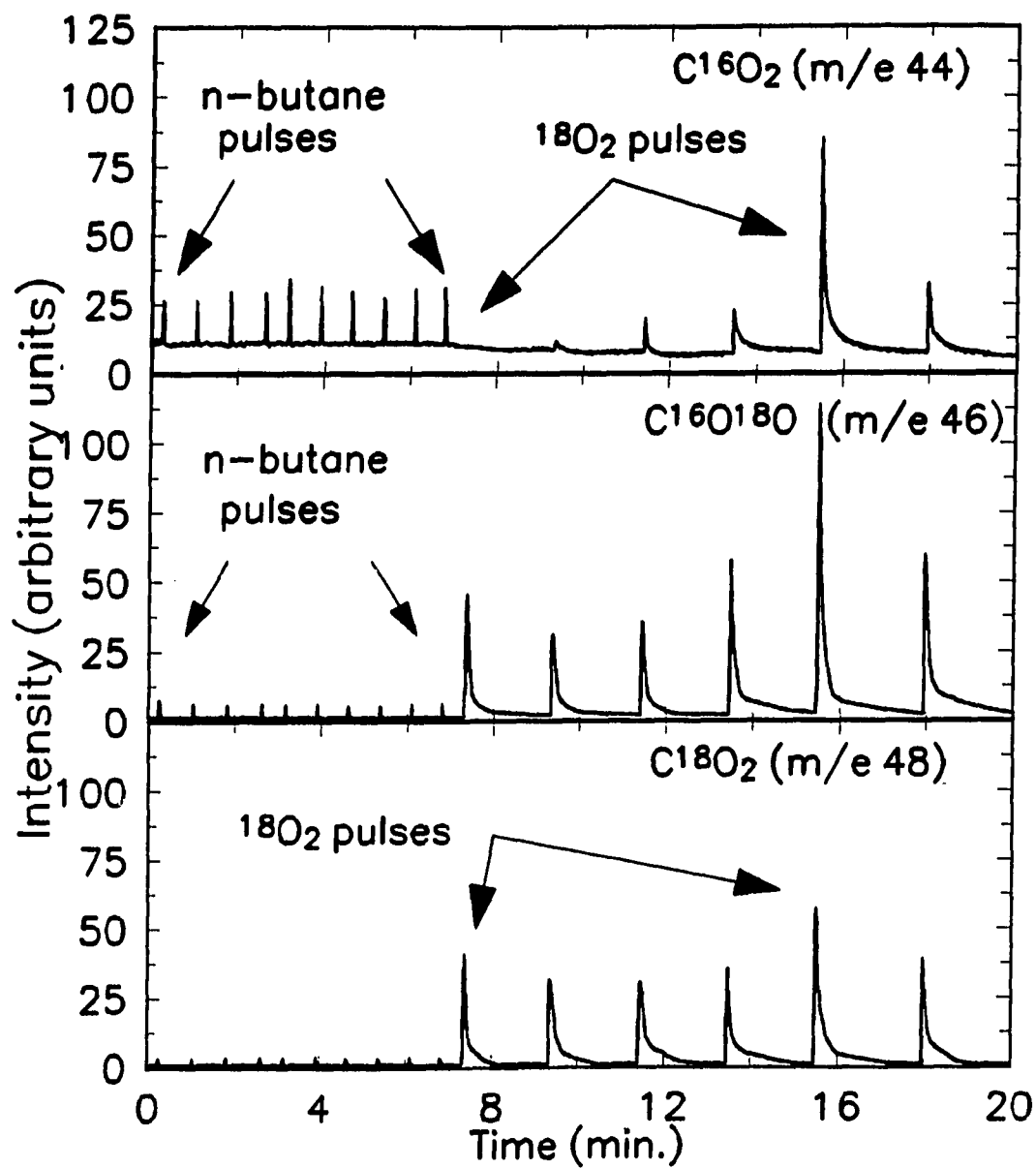


Figure 4: Carbon dioxide production during the reoxidation of the catalyst by $^{18}O_2$ pulses following ten consecutive n-butane pulses

However, the production of $C^{18}O_2$ in comparable quantity to that of $C^{16}O^{18}O$ during the first ^{18}O pulse once again confirms that along with the initial catalyst reoxidation process, an adsorbed dioxygen species is involved in the combustion process which occurs parallel to the reoxidation. Centi et al. [14] have observed similar results during their n-butane/ ^{18}O co-feed experiment with $(VO)_2P_2O_7$ catalyst. Based on these results, they have proposed an chemisorbed oxygen species responsible for direct combustion of n-butane to CO_2 . This similarity indicates that these two species are most likely identical one.

Thus, there are at least two routes for carbon oxide formation other than the consecutive oxidation of maleic anhydride. First one consists of direct combustion of n-butane by an adsorbed dioxygen species. The second one involves the complete oxidation of the partially oxidized surface hydrocarbon species. Two different oxygen species seems to be competing in this process. One of them, as could be expected is the short-lived adsorbed dioxygen species. The other species is either an irreversibly chemisorbed oxygen species or a low concentration surface layer oxygen species.

Alternate 1-Butene/ O_2 Pulses

Alternate hydrocarbon/oxygen studies were also carried out with 1-butene. The results of studies with ^{16}O are presented in Figure 5. General characteristics of CO_2 transience are similar to that observed with n-butane. However, unlike n-butane where prolonged tailing was observed for CO_2 produced during oxygen pulse, CO_2 peaks observed for 1-butene studies are remarkably sharp. This should be expected since n-butane is known to be very

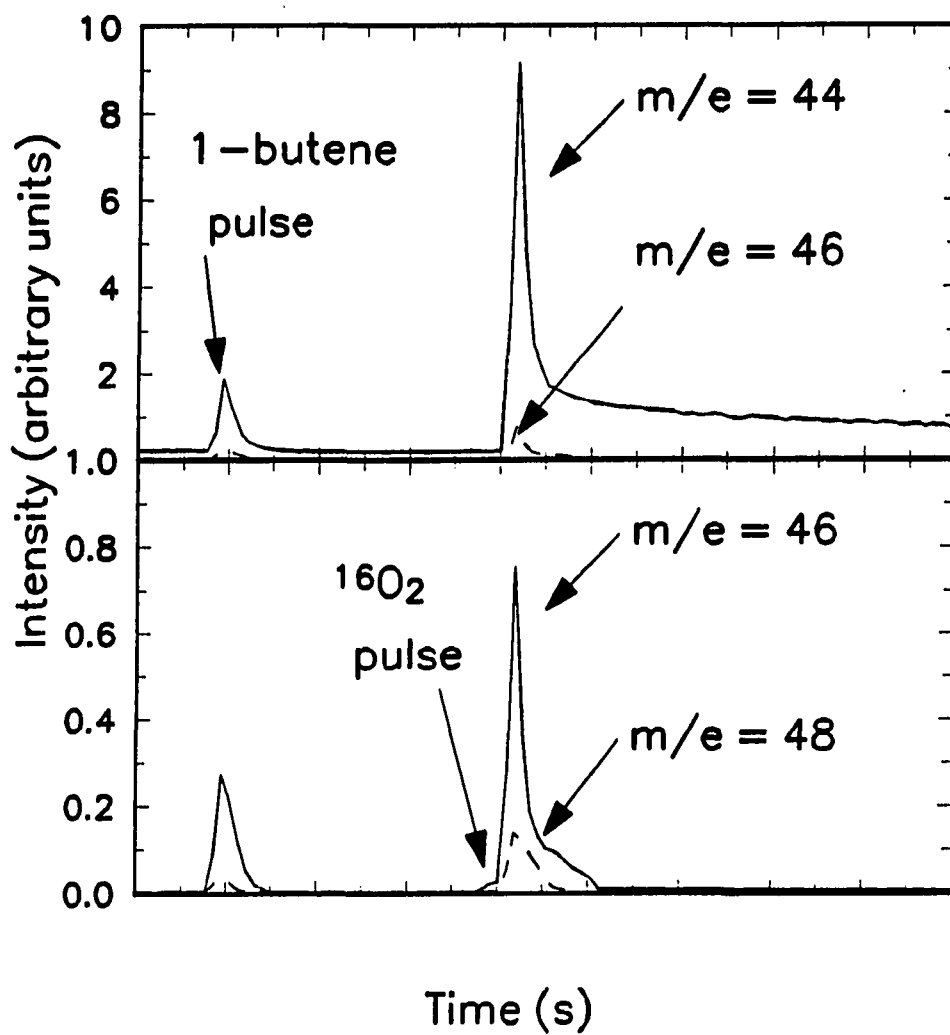


Figure 5: Carbon dioxide production during the alternate 1-butene/¹⁶O₂ pulses

strongly adsorbed, which would explain the tailing observed. More subtle differences are observed in the results of the ^{18}O studies. These results are shown in Figure 6. All the three CO_2 peaks (m/e 44, 46 and 48) for 1-butene are sharper and show much less tailing as compared to those observed during n-butane studies. The sharpness of the CO_2 peaks observed in the case of 1-butene can be expected, since the surface hydrocarbon intermediate will be more dehydrogenated as compared to that in the case of n-butane.

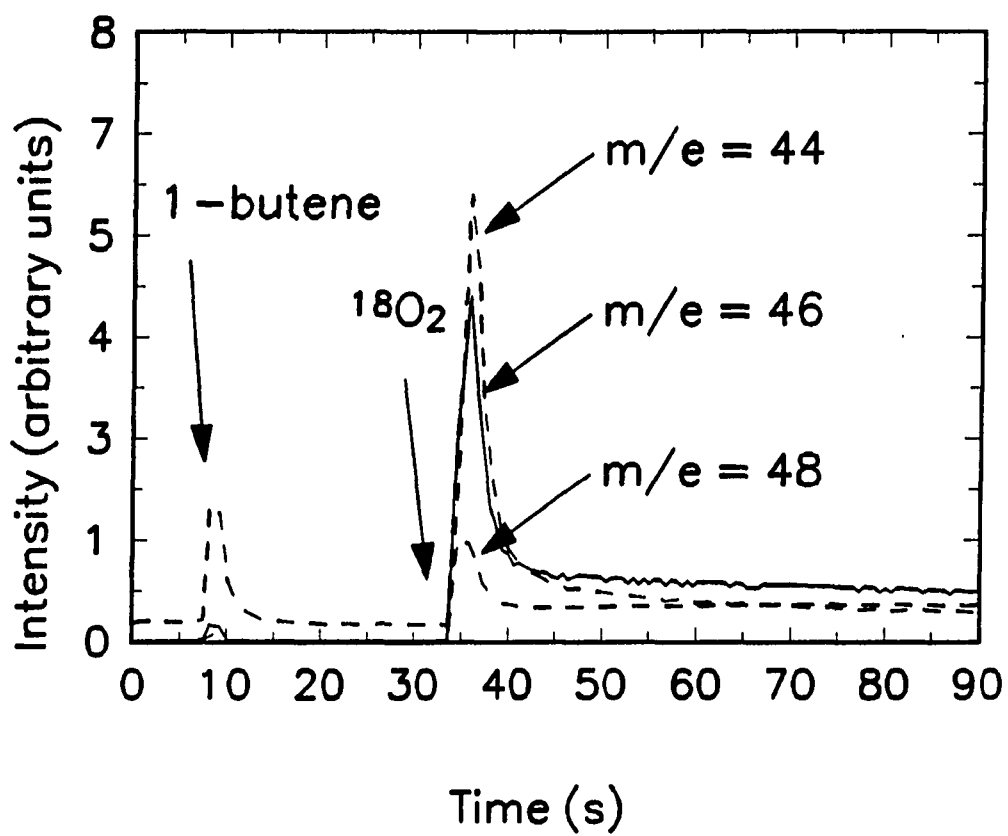


Figure 6: Carbon dioxide production during the alternate 1-butene/ $^{18}\text{O}_2$ pulses

CONCLUSIONS

Alternate C₄ hydrocarbon/O₂ pulse studies with ¹⁸O-labeled (VO)₂P₂O₇ catalyst allowed to investigate the nature of surface hydrocarbon intermediate formed during the n-butane oxidation. These studies indicated that this intermediate is strongly (irreversibly) chemisorbed, and is already significantly oxidized. Both short-lived adsorbed dioxygen and irreversibly chemisorbed oxygen can completely oxidize it to carbon oxides. However, surface layer oxygen is not capable of completely oxidize it. Furthermore, the oxidation of this intermediate seems to be a stepwise process. First, the gas-phase oxygen reoxidize the reduced catalyst sites, and either these oxidized sites or irreversibly chemisorbed oxygen oxidize this surface hydrocarbon intermediate to carbon oxides. For 1-butene, similar results were observed, however, the surface hydrocarbon intermediate in this case is highly oxidized.

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SUMMARY AND RECOMMENDATIONS

General Summary

A modified isotopic reactive-site mapping (IR-SM) approach was successfully employed to study the redox mechanism for the conversion of n-butane to maleic anhydride over $(VO)_2P_2O_7$ catalyst. The modification involved quantifying the yields of the oxidation products. These studies thus allowed to determine not only the nature of the reactive sites but also their availability for the selective and nonselective pathways.

To employ the IR-SM approach, it is essential to prepare a catalyst labeled with ^{18}O at specific lattice sites. This was achieved for $(VO)_2P_2O_7$ catalyst by using a three-stage solid state based synthesis procedure, which exploited the reversible redox between β - $(VO)_2P_2O_7$ and β - $VOPO_4$. The distribution of ^{18}O labeling in the lattice sites of $(VO)_2P_2O_7$ was determined by characterizing this catalyst by infrared and Raman spectroscopies, along with other complimentary techniques. This evidence pointed to a highly site-specific ^{18}O incorporation at P-O lattice positions. Results of the anaerobic C_4 hydrocarbon pulse reactor studies with this catalyst allowed to associate specific reactive sites with individual mechanistic steps involved in the selective and nonselective pathways.

For selective conversion, n-butane is chemisorbed and activated at the vanadyl dimer sites of $(VO)_2P_2O_7$ catalyst in an irreversible and very specific manner to form a partially dehydrogenated olefinic surface intermediate. This species then undergoes ring oxygen

insertion at a nearby V-O/^P-V site thereby achieving a C_{2v} symmetry. Under oxygen deficient conditions, this surface species may desorb as furan. However, when additional nearby P-O-V sites are available, it can undergo additional reaction and oxygen insertion at this sites which leads to the production of maleic anhydride. At least two nonselective pathways were evident for carbon oxide formation: either by the direct combustion of n-butane, first involving its cracking at the highly electrophilic V=O sites or by the consecutive oxidation of maleic anhydride formed. Alternate C₄ hydrocarbon-oxygen studies allowed to investigate the nature of the hydrocarbon intermediate formed during the nonselective activation of n-butane. This intermediate was found to be strongly (irreversibly) chemisorbed, and was already significantly oxidized. Both short-lived adsorbed dioxygen and irreversibly chemisorbed oxygen was found capable of oxidizing it further to carbon oxides.

Participation of bulk oxygen in the oxidation mechanism was found to be very limited. Rather, the redox was determined to involve only a few near surface layers.

A comparison of ¹⁸O incorporation in the products of n-butane and 1-butene gave important information regarding the C₄ hydrocarbon oxidation in general. It was evident from these studies that the selectivity of a reactive site depends upon the reactivity of the hydrocarbon feed, and thus, a surface sites may have different functions in different C₄ hydrocarbon oxidation. Furthermore, the initial interaction of n-butane seems to be fundamentally different than that of 1-butene. Thus, the IR-SM technique is a potentially powerful method for probing the nature and the availability of the reactive surface sites of other selective oxidation catalysts.

Recommendations for Future Work

This investigation have provided valuable information regarding the nature of the redox mechanism for the oxidation of C₄ hydrocarbons over (VO)₂P₂O₇ catalyst. These results coupled with the current understanding of this system provides new questions to be answered. Some of these potential research areas are mentioned below.

- [1] This study emphasize the reactivity of surface layer sites of a fresh catalyst under anaerobic conditions. However, adsorbed oxygen is also known to play crucial role in this mechanism. It is therefore desirable to modify the IR-SM method so as to determine the exact nature of the chemisorbed oxygen and its function in the redox mechanism.**
- [2] It is clear from these studies that this reaction is surface plane sensitive. It therefore provides unique opportunity to study its structure sensitivity in detail. This can be achieved by synthesizing single crystals with preferred orientations [020] and [204]. The catalytic performance testing and other fundamental studies can be then carried out with these catalyst to gain important basic knowledge regarding the C₄ hydrocarbon oxidation on metal oxides.**
- [3] These studies also showed that a specific geometry of vanadyl dimers along with the rest of the P-O-V sites as provided by [020] plane is essential for high selectivity of these catalysts. Transition metal pyrophosphates are known to provide this geometry. It is therefore logical to study other similar pyrophosphates such as that of Mo, W and Fe. Rather, these pyrophosphates provide unique opportunity to study the influence of oxidation state, metal cation and metal-oxygen bond strength on the catalyst activity.**

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